46 h according to the general procedure. The crude product was purified by short column chromatography on silica gel.

The ^1H NMR ($CDCl_3$/100 MHz) spectrum of the product showed the triplet assigned to the endo-3-H at δ 1.75 (J = 2.5 Hz), and these spectral data together with melting points were in full accord with the literature.[16]

Reduction of Acyl Chlorides: General Procedure. To a refluxing solution of DMBI (2.4 mmol) in acetonitrile (5 mL) was slowly added a mixture of acyl chloride (2.4 mmol) and acetic acid (2.4 mmol) in acetonitrile (5 mL) dropwise under stirring. After refluxing had been continued for the appropriate time (see Table VI), the reaction mixture was cooled in an ice bath and poured into cold $NaHCO_3$ solution. The aqueous solution was extracted with chloroform and the extract dried with Na_2SO_4. The crude product obtained by evaporation of chloroform was subjected to short column chromatography on silica gel to give pure product.

Identification of products was performed by comparison of NMR, IR, and MS spectra and melting points of 2,4-dinitrophenylhydrazone derivatives of the isolated products with those of corresponding authentic samples. The spectral and physical data were in satisfactory agreement.

Reduction of Benzoyl Chloride with DMBI-*2-d*. Benzoyl chloride was treated with an equimolar amount of DMBI-*2-d* for 2 h according to the general procedure. The crude product was purified by short column chromatography on silica gel to give fully deuteriated benzaldehyde-*d*; no aldehyde proton absorption was detected by ^1H NMR analysis.

Registry No. **1a**, 70-11-1; **1b**, 532-27-4; **1c**, 450-95-3; **1d**, 99-73-0; **1e**, 2491-38-5; **1f**, 42330-10-9; **1g**, 3212-63-3; **1h**, 822-85-5; **1i**, 31236-94-9; **1j**, 76-29-9; **2a**, 51075-28-6; **2b**, 19261-37-1; **2c**, 51075-29-7; **2d**, 35066-22-9; **3a**, 5437-45-6; **3b**, 140-18-1; **3c**, 3017-53-6; **3d**, 81577-34-6; **3e**, 535-11-5; **3f**, 869-10-3; **4**, 5061-21-2; **5a**, 79-08-3; **5b**, 79-11-8; **5c**, 2623-82-7; **6**, 141-28-6; **7**, 7209-01-0; DMBI (X = 5-H), 3652-92-4; DMBI (X = 5-OMe), 105282-67-5; DMBI (X = 5-Me), 105282-68-6; DMBI (X = 5-I), 105282-69-7; DMBI (X = 5-NO_2), 14443-02-8; DMBI-2-*d* (X = 5–H), 105282-70-0; $PhCOCH_3$, 98-86-2; *p*-$BrC_6H_4COCH_3$, 99-90-1; *p*-$HOC_6H_4COCH_3$, 99-93-4; $(Pr)_2CO$, 123-19-3; $(i\text{-}Pr)_2CO$, 565-80-0; $PhCH_2CH_2CH_3$, 104-53-0; $PhCH(CH_3)CHO$, 93-53-8; $CH_3(CH_2)_6CHO$, 124-13-0; $PhCH_2OCOMe$, 140-11-4; $PhCH_2OCOEt$, 122-63-4; EtOCOEt, 105-37-3; $CH_3(CH_2)_6CO_2H$, 124-07-2; CH_3CO_2H, 64-19-7; PhCOCl, 98-88-4; *p*-$O_2NC_6H_4COCl$, 122-04-3; *p*-$MeOC_6H_4COCl$, 100-07-2; $CH_3(CH_2)_6COCl$, 111-64-8; PhCDO, 28106-59-4; *p*-$O_2NC_6H_4CHO$, 555-16-8; *p*-$MeOC_6H_4CHO$, 123-11-5; 1-methyl-2-phenylbenzothiazoline, 16192-33-9; 2-phenyl-3-methylbenzoxazoline, 16192-26-0; 2-phenylbenzimidazoline, 53088-00-9; 2-phenylbenzothiazoline, 31230-83-8; cyclohexanone, 108-94-1; cyclododecanone, 830-13-7; camphor, 76-22-2; dihydro-2-furanone, 96-48-0; cyclohexanecarbonyl chloride, 2719-27-9; cyclohexanecarboxaldehyde, 2043-61-0.

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An Enolized Sulfonamide Formed by Strong Hydrogen Bonding to Triphenylphosphine Oxide

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Compound I, 5-methyl-6-phenyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide, exists in chloroform solution and in crystals grown from chloroform as an amide with NH···O=C intermolecular hydrogen bonds. In the presence of triphenylphosphine oxide [(TPP)O], I tautomerizes to an enol form and complexes with (TPP)O through a very strong hydrogen bond between the phosphoryl oxygen and the enol OH group. In solution and in the solid state the complex exhibits unusually low-frequency OH stretching bands in its infrared spectrum, consistent with the observed hydrogen-bond distance of 2.504 (3) Å [O(H)···O=P], determined from crystal structure analysis. The crystal structures of I and its complex with (TPP)O, II, and the infrared and NMR spectra of I and II are reported. Comparison of solution- and solid-state structures are made, and an analysis of the role of intermolecular hydrogen bonds in the formation of tautomers of I is given.

Hydrogen bonds can be used to orient molecules into predictable aggregate patterns in solution or in the solid state, analagous to the role of single bonds in determining the pattern of functional groups within molecules.[1] Being able to predict which of several possible intermolecular hydrogen bonds will form when multiple hydrogen bond acceptor and donor sites are present in a molecule is of fundamental importance to controlling the structure of molecular aggregates in solution and, ultimately, to determining the structure of nucleation sites for crystal growth.[2]

Usually the process of forming intermolecular hydrogen bonds does not involve intramolecular rearrangement of the complexing species, although conformational changes may be observed,[3] and bond lengths and angles will be altered near the hydrogen-bond site.[4] Benzamide, for

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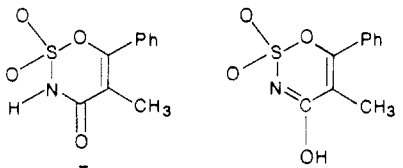
0022-3263/86/1951-5405$01.50/0

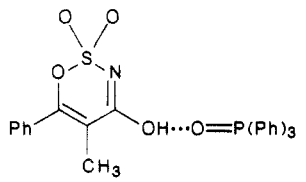
example, can be crystallized as a dimer with NH···O= hydrogen bonds[5] or can be cocrystallized with carboxylic acids such that the NH proton is hydrogen bonded to the acid carbonyl group.[6] The molecular structure of benzamide is not affected by this change in hydrogen-bond pattern.

The enolizable compound, I, can selectively be induced to adopt its enol form, Ia, or its keto form, Ib, both in



Ia

Ib



II

solution and in the solid state by controlling the type of proton acceptors available for intermolecular hydrogen-bond formation. Ib forms in the presence of (TPP)O, giving rise to a complex that has a short intermolecular hydrogen bond between the phosphoryl oxygen and the OH group of Ib. Ia forms in the absence of (TPP)O and is stabilized in the solid state by formation of intermolecular hydrogen bonds between the acyl sulfonamide NH group and its carbonyl group. Crystal structures were done to confirm the existence of these two forms and to allow the assignment of solution structures from comparisons of solution- and solid-state infrared spectra.

Experimental Section

Synthesis of 5-Methyl-6-phenyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-Dioxide (I). Oxathiazine dioxide I was prepared by reaction of propiophenone and chlorosulfonyl isocyanate in diethyl ether solvent according to the published procedure.[7] Single crystals were grown from ethanol as large clear prisms.

Preparation of II, the 1:1 Complex of Triphenylphosphine Oxide and I. I (2.39g, 0.01 mol) and triphenylphosphine oxide (2.78 g, 0.01 mol) were heated at reflux in toluene (25 mL) for 1.5 h, cooled to room temperature, filtered, and allowed to stand at about 5 °C to slowly precipitate complex II as colorless crystals: 3.28 g (63.4%); mp 126–127.5 °C. Anal. Calcd for $C_{28}H_{24}O_5NSP$: C, 64.99; H, 4.68; N, 2.71. Found: C, 65.14; H, 4.73; N, 2.70.

Infrared Spectra. Infrared spectra of compounds I and II were obtained from KBr pellets and from chloroform solutions on a Nicolet 7199 FT IR spectrometer and a Perkin-Elmer 283 spectrometer. The solution- and solid-state infrared patterns of I are very similar, showing a broad NH stretching absorption at 3100 cm^{-1} and the amide carbonyl band at 1690 cm^{-1} (Figure 1a). Figure 1b shows a distinctly different pattern for (TPP)O complex II, particularly in the hydrogen-bond stretching region from 1700 to 2500 cm^{-1} where broad multiple bands occur. These bands are at much lower wavenumbers than usual NH or OH stretching bands, indicating the presence of an unusually strong hydrogen bond.

The carbonyl band occurring at 1690 cm^{-1} in solution- and the solid-state spectra of I is not present in the solid-state spectrum of the complex (Figure 1b). A strong absorption at 1625 cm^{-1}, characteristic of the complex, is probably due to the C=N

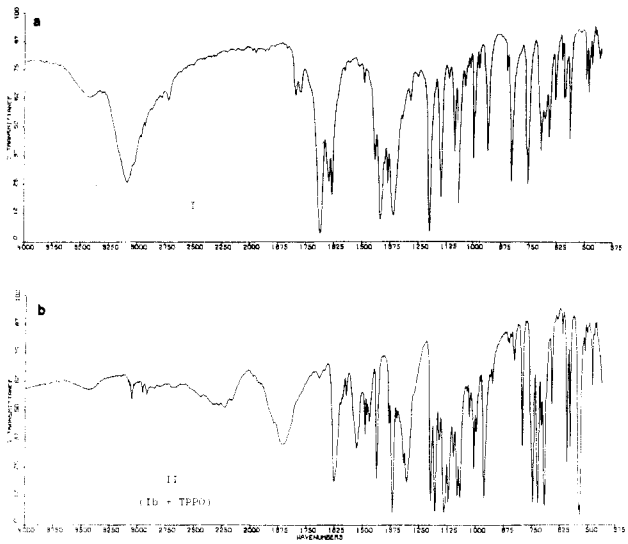


Figure 1. Solid-state infrared spectra: (a) I (KBr disk), a hydrogen-bonded sulfonamide dimer showing a carbonyl stretching band at 1690 cm^{-1} characteristic of the hydrogen-bonded keto group. (b) II (KBr disk), a hydrogen-bonded complex of the enol form of I and triphenylphosphine oxide showing low-frequency OH stretching bands around 1850 cm^{-1} characteristic of strong hydrogen bonds. In II, the strong hydrogen bond occurs between the enol OH hydrogen and the phosphoryl oxygen. The absence of a 1690-cm^{-1} band is consistent with the loss of the keto carbonyl function upon enolization and complexation.

stretching band. (TPP)O itself is transparent between 1600 and 2900 cm^{-1}.

The solution spectrum of the complex of I and (TPP)O looks like a composite spectrum of the two solid-state spectra shown in Figure 1, consistent with the presence of both enol and keto forms of I in solution. The 1690- and 1625-cm^{-1} bands occur with approximately equal intensities over a concentration range of 1.0–to 0.1 M in chloroform.

NMR. Solution ^1H NMR and ^{31}P NMR spectra were obtained from deuteriochloroform on either a Varian XL100 or XL200 instrument. The spectra of I and II give the following peaks (ppm). I: ^1H NMR ($CDCl_3$) 2.12 (s, 3), 7.44–7.64 (m, 5), 9.85 (br s, 1). II: ^1H NMR ($CDCl_3$) 2.05 (s, 3), 7.38–7.90 (m, 15), 12.70 (br s, 1); ^{31}P NMR ($CDCl_3$) 33.2 (downfield from H_3PO_4). The low-field proton signal at 12.70 ppm in the spectrum of II is typical of strongly complexed protons.

X-ray Structure Analyses. I: a = 7.896 (2), b = 7.985 (2), c = 17.024 (5) Å; orthohombic; $P2_12_12_1$; Z = 4, ρ_{calcd} = 1.486; μ = 26.6 cm^{-1}; crystal size, 0.20 × 0.34 × 0.54 mm^3; $C_{10}H_9NSO_4$; MW 239.24; 1309 unique reflections ($+h,k,l$).

II: a = 11.177 (2), b = 8.659 (3), c = 26.377 (4) Å; β = 100.24 (I)°; monoclinic; $P2_1/c$; Z = 4; ρ_{calcd} = 1.36g/cm^3; μ = 20.2 cm^{-1}; crystal size 0.30 × 0.24 × 0.12 mm^3; $C_{28}H_{24}SO_5NP$; MW 512; 3130 unique reflections ($\pm h,k,l$).

Structure solution of I and II proceeded normally.[8]

Results and Discussion

The acyl sulfonamide, I, which is structurally related to the sweeteners saccharin and acesulfame K (a Hoechst

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(8) Crystal data for I and II were collected on an Enraf-Nonius CAD-4 diffractometer using Cu Kα radiation. Both structures were solved by MULTAN direct-methods programs from the SDP structure solution package.[9] All non-hydrogen atoms were found on the first E-maps, and hydrogen atoms were found in a difference Fourier map. Hydrogen atoms were refined isotropically with B values of 6.0 Å^2 for I and 8.0 Å^2 for II. For structure I, 1207 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement. For II, 2218 reflections with $I > 3\sigma(I)$ were used. Final R factors were 0.051 (R_w = 0.062) for I and 0.059 (R_w = 0.059) for II, with $w = 1/\sigma^2(F_o)$. Final atomic positional and thermal parameters and unit cell stereoviews are available as supplementary material. Structure factor tables and tables of inter- and intramolecular bond lengths and angles are available from the author.
(9) Frenz, B. A. *Enraf-Nonius Structure Determination Package*, 3rd ed.; Enraf-Nonius: Delft, Holland, 1978.

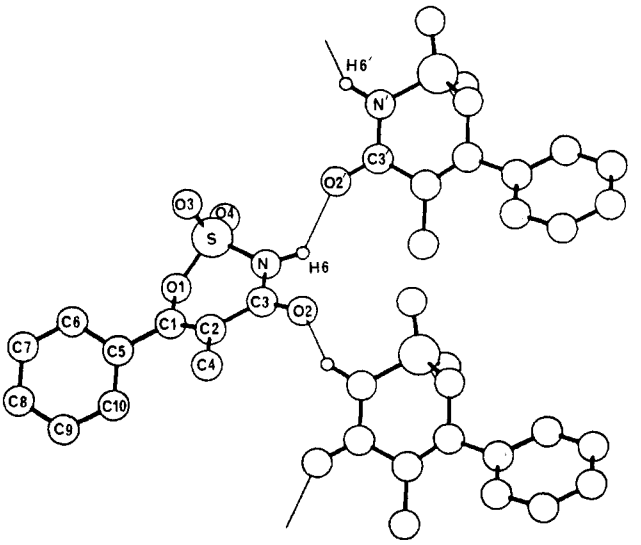


Figure 2. ORTEP drawing of three screw-related molecules from the crystal structure of Ia, showing the hydrogen-bond interaction between the amide NH of one molecule and the carbonyl oxygen of a neighbor.

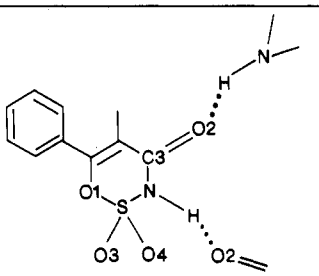
trademark),[10] was shown to be capable of tautomerism in solution and in the solid state. It exists in the keto form, Ia, in chloroform solution and in crystals grown from chloroform, but it exists in the enol form, Ib, in solutions containing (TPP)O and in crystal complexes with (TPP)O. The role of (TPP)O in inducing I to enolize involves formation of a very strong hydrogen bond between the enol OH of Ib and the phosphoryl oxygen of (TPP)O. This strong intermolecular hydrogen bond is formed in competition with intermolecular bonding between the NH and >C=O of Ia, a type of interaction normally found for amide compounds.[11]

The two different crystal structures of I provide us with a unique opportunity to study the relationship between molecular tautomerism and intermolecular hydrogen-bond formation. For the molecule Ia, there is one proton donor group (the NH group) and there are three potential proton acceptor groups (the carbonyl oxygen and the two exocyclic oxygens of the OSO_2 group) available for hydrogen-bond formation. Crystallization of Ia involves competition between the acceptor groups for the single proton donor, and in the observed crystal structure it is found that it is the carbonyl oxygen that is hydrogen bonded to the amide NH, shown in Figure 2. The intermolecular NH···O bond length is 2.780 (3) Å, 0.2 Å shorter than comparable bond lengths for normal amides, with the stronger bond resulting from increased acidity of the amide NH due to the neighboring electronegative OSO_2 group. The intramolecular N···C(3) and C(3)···O(2) bond lengths [1.389 (3), 1.220 (3) Å] are consistent with normal amide structures and show that I is in the keto form.

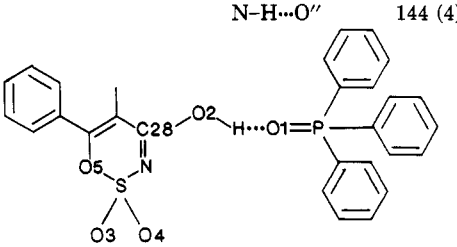
When I crystallizes in the presence of (TPP)O, it enolizes and forms a 1:1 complex, II. The enol form, Ib, has the OH group as the only proton donor and has the imine nitrogen and the SO_2 oxygens available as potential proton acceptors. Nevertheless, intermolecular hydrogen bonds do not form between molecules of Ib but form only between the OH of Ib and the phosphoryl oxygen of (TPP)O. In the crystal structure of II, the enol form of I is clearly established since N(1)···C(28) and C(28)···O(2) intramolecular bond lengths are 1.306 (4) and 1.312 (4) Å. The enol assignment is also confirmed by the position of the proton located 1.10 (5) Å from the O(2) oxygen with a C(28)–O(2)–H bond angle of 162 (4)°.

The most striking feature of the structure, however, is the presence of an extremely short intermolecular hydrogen bond between the OH of I and the phosphoryl oxygen of (TPP)O. The O(1)···O(2) distance is only 2.504 (3) Å with H···O(1) = 1.44 (5) Å, shown in Figure 3. The phosphoryl P=O bond length is 1.501 (2) Å, considerably longer than the comparable bond in (TPP)O itself [1.46 (1) Å[12]], but at the average value found for other (TPP)O complexes (1.50 Å).[13] The unusual strength of this hy-

Table I. Selected Bond Lengths (Å) and Angles (deg)[a]



	length		angle
S–O1	1.578 (2)	O1–S–O3	109.0 (1)
S–O3	1.414 (2)	O1–S–O4	107.0 (1)
S–O4	1.406 (2)	O1–S–N	99.1 (1)
S–N	1.626 (2)	O3–S–O4	120.2 (2)
O1–C1	1.409 (3)		
O2–C3	1.222 (3)		
N1–C3	1.386 (3)	N–C3–O2	118.2 (2)
C1–C2	1.345 (3)	N–C3–C2	118.1 (2)
C1–C5	1.473 (3)	C3–C2–C1	120.8 (2)
N–H	0.79 (5)		
O2···N′	2.780 (3)	C1–O1–S	119.6 (1)
O2···H	2.10 (4)	C3–O2···N′	147.2 (2)
		N–H···O″	144 (4)



	length		angle
S–O3	1.417 (3)	O5–S1–N1	104.2 (2)
S1–O4	1.410 (3)	O3–S1–O4	118.0 (2)
S1–N1	1.580 (3)	S1–N1–C28	116.4 (3)
N1–C28	1.306 (4)	N1–C28–O2	120.0 (3)
C28–O2	1.312 (4)	N1–C28–C26	125.6 (3)
O2–H1	1.10 (5)	C28–C26–C25	118.5 (3)
C28–C26	1.457 (5)	C26–C25–O5	119.8 (3)
C26–C27	1.508 (5)	C25–O5–S1	116.2 (2)
C26–C25	1.336 (5)		
C25–C19	1.471 (5)	O1···H1–O2	162 (4)
O5–S1	1.619 (3)		
H1···O1	1.44 (5)	C1–P1–O1	114.0 (2)
O2–O1	2.504 (3)	C1–P1–C7	108.2 (2)
O1–P1	1.493 (3)	C1–P1–C13	106.3 (2)
P1–C1	1.783 (4)	C13–P1–O1	109.7 (2)
P1–C7	1.804 (4)	C13–P1–C7	107.7 (2)
P1–C13	1.789 (4)	C7–P1–O1	110.7 (2)

[a] N′ is from a symmetry-related molecule at $1-x, -{}^1/_2+y, {}^3/_2-z$. O″ is from a symmetry-related molecule at $1-x, {}^1/_2+y, {}^3/_2-z$.

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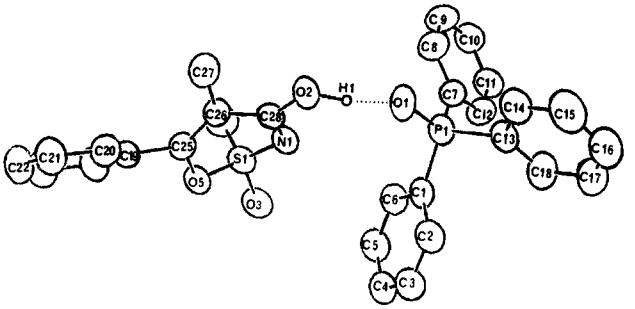

Figure 3. ORTEP drawing of the molecular complex of Ib and (TPP)O showing the short hydrogen bond between OH and the phosphoryl oxygen.

drogen bond also manifests itself in the solid-state IR spectrum of II (Figure 1b), which shows Hadzi type II OH stretching bands[14] extending from 2000 to 1700 cm^{-1}. The ability of phosphoryl groups to form very strong hydrogen bonds with P=O···(H)O distances of 2.55 Å or less has also been seen for the complex of (TPP)O with trichloroacetic acid[20] and more recently for 1,8-biphenylenediol and hexamethylphosphoramide where the phosphoryl oxygen forms short bifurcated hydrogen bonds to both OH groups of one molecule simultaneously.[21]

The complex II was also seen to exist in solution. Since we knew the crystal structures of I and II, assignment of solution structures could be made by comparison of solution- and solid-state IR spectra. In the absence of (TPP)O, the solution spectrum of I matches that of the solid-state spectrum of Ia. When (TPP)O is present in solution with I, the appearance of bands due to the keto and to the complexed enol form are both observed. In particular, the unusual low-frequency OH stretching bands associated with the short phosphoryl hydrogen band are present. ^1H NMR spectra of solutions of I and (TPP)O show a peak at 12.70 ppm for the hydrogen-bonded proton, a position indicative of extensive deshielding due to strong hydrogen bonding. These solution studies show that the hydrogen bond between Ib and (TPP)O is an inherent property of the molecular complex and not just a result of unusual crystal-packing forces.

The structure of the (TPP)O molecule observed in crystals of II also bears comment since it is in a conformation that represents a stabilized transition state where the interplanar dihedral angles between the three phenyl rings are 90, 8.6, and −15.4°. Dunitz has shown that for the 1114 known crystal structures containing triphenylphosphine groups the average conformation is a symmetric three-bladed propeller with each phenyl group rotated from its C–P–X plane by 40°.[13] The transition state that obtains during conversion of enantiomeric conformers involves a postulated transition state with the three dihedral angles equal to 90, 10, and −10°, nearly identical with those found in the structure of II.

From the observed crystal structures of I and II, and from their deduced solution structures, it is seen that the phosphoryl oxygen is the strongest proton acceptor available. In the absence of (TPP)O a normal amide intermolecular hydrogen-bond pattern occurs, but in the presence of (TPP)O, enolization of I takes place in order to establish an extremely strong intermolecular hydrogen bond. Analysis of molecular models does not reveal any obvious steric constraints preventing hydrogen-bond formation between the amide NH of the keto form and the phosphoryl oxygen. It is also known from other structures that phosphoryl groups can hydrogen bond to NH groups.[22] A possible explanation for the enolization of I is that the complexation mechanism involves deprotonation of Ia by (TPP)O to form a nitrogen anion that rearranges to a more stable oxygen anion. Complex formation then occurs upon reprotonation of the anion by $(TPP)OH^+$. The NH proton of Ia should be more acidic, and thus more labile than normal amides due to the presence of the neighboring OSO_2 group. Work is continuing in our laboratory to determine whether other proton acceptors of varying basicities are also capable of inducing I to enolize and whether other amides can be enolized in the presence of strong proton acceptors.

Conclusions

Triphenylphosphine oxide and I form a 1:1 complex that is stabilized by a very short hydrogen bond of 2.504 (3) Å between the phosphoryl oxygen and the enolized oxygen of the oxathiazine amide group. The uncomplexed oxathiazine compound exists in the crystalline state and in solution as a normal, keto-type, amide group that enolizes only when it complexes with the strong oxide acceptor. The very strong bond strengths associated with this interaction are confirmed by the observation of Hadzi type II infrared patterns and by a large downfield NMR shift for the hydrogen-bonded proton in the complex.

Note Added in Proof: Prof. Fred Hassner informed us by letter on Oct. 30, 1986, that Prof. Victor Day had studied the structure of II in 1974. The ORTEP view provided to us by F.H. is essentially the same as that in our Figure 3. We thank F.H. for informing us of this unpublished data.

Supplementary Material Available: Stereoviews and listings of positional parameters and temperature factors for I and II (12 pages). Ordering information is given on any current masthead page.

(14) (a) Hadzi, D. *Pure Appl. Chem.* **1965**, *11*, 435. (b) Very strong hydrogen bonds, where O···O distances are <2.5 Å exist in a variety of inorganic complexes such as hydrogen dinitrate[15] and in some organic salts such as $[(TPP)O)_2H^+]_2[CuCl_4^{2-}]$.[16] These complexes are called homoconjugate[17] since the hydrogen is bonded to two identical centers, viz. $[AHA]^+$. The structure of II presented here is an example of a neutral heteroconjugate system, [AHR], a type of complex recently described by Emsley.[18] For an excellent review of the special physical and spectroscopic properties associated with very strong hydrogen bonds, see Emsley's review: ref 19.

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