Dialkyl Sulfone Diimines. Synthesis, Raman Spectra, Chemical and Physical Properties

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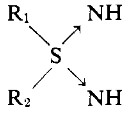
Abstract: An improved synthesis of the recently described dialkyl sulfone diimines[1,2] in acetonitrile is described. Reaction of chloramine–ammonia with dialkyl sulfides in 2-propanol has been shown to yield sulfoxide and sulfone imine by-products, as well as sulfone diimines. Their formation is best accounted for by assuming that displacement of sulfur on chloramine occurs to some extent on chlorine, as well as on nitrogen. The crystalline and aqueous solution Raman spectra of dimethyl, diethyl, and methyl dodecyl sulfone diimine have been measured and are shown to be consistent with tetrahedral bonding for sulfur (C_{2v} local symmetry). Tentative band assignments are presented based on comparison with analogous compounds and the Raman spectra of dimethyl sulfide, diethyl sulfide, and dimethyl sulfone imine. Characteristic vibrational bands for $R_2S(NH)_2$ are tabulated and the spectral evidence for hydrogen bonding of this new semipolar group is discussed. The sulfone diimines were shown to be considerably more stable thermally than sulfimines but less stable than sulfoxides. Hydrolysis by acid or base catalysis could not be effected, although decomposition *via* other routes occurred in acid.[2] The basicity and metal complexing abilities of sulfone diimines parallel those of amine oxides, except toward silver. Silver ion reacts in aqueous solution with the formation of a precipitate and a decrease in pH to 2–3.

Cogliano and Braude[1] recently isolated from the reaction of chloramine with dialkyl sulfides a new class of compounds to which they assigned structure II.



I

$[R_2\overset{+}{S}—NH\overset{-}{N}H]_2$

II

The alternative structure, I, was recently proposed by Appel, *et al.*,[2] for these compounds, on the basis of their inertness toward oxidizing agents, the absence of hydrazine or nitrogen in the hydrogen chloride cleavage products, and mass spectral studies. The present work provides further support for structure I derived from Raman and infrared spectral studies, an improved synthesis, new information regarding the chemistry involved in the synthesis, and some further chemical and physical properties of sulfone diimines.[3]

Synthesis

The sulfone diimines are best synthesized by allowing the dialkyl sulfide to react with excess chloramine and ammonia[5] in acetonitrile.[2] They are easily isolated in 45% yields as the free base by solvent extraction from the ammonium chloride.[6]

Acetonitrile is superior to 2-propanol[1,2] as a reaction medium because reaction in the latter solvent produces several previously unrecognized by-products.[7] For example, methyl dodecyl sulfide in 2-propanol yields, in addition to sulfone diimine, the sulfone imine (6%), sulfoxide (1%), 1-dodecene (10%), and dodecanenitrile (1%). The olefin and nitrile are formed in either solvent. Unfortunately, methyl tetradecyl and hexadecyl sulfides crystallize from acetonitrile at low temperatures, necessitating the use of 2-propanol for these homologs and resulting in more difficult purification.

The formation of the product by a sequence of nucleophilic displacement reactions on the nitrogen of chloramine has been suggested.[1,2] Further evidence for intervention of a sulfimine intermediate is isolation of the olefin and nitrile, which are likely decomposition products of sulfimines.[4,8] The conditions encountered during work-up were too mild for the olefin and nitrile to have been formed from the diimine.

The formation of sulfoxide and sulfone imine suggests that nucleophilic attack of sulfur on chloramine occurs to some extent on chlorine as well as on nitrogen, as is the case with other nucleophiles.[9] Displacement by the dialkyl sulfide on chlorine would yield a dialkylchlorosulfonium ion, R_2S^+Cl, which would be expected to undergo alcoholysis to sulfoxide. Displacement by the sulfur atom of the sulfimine on chlorine would yield

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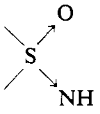
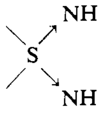
(1) J. A. Cogliano and G. L. Braude, *J. Org. Chem.*, **29**, 1397 (1964).

(2) R. Appel, H. Fehlhaber, D. Hänssgen, and R. Schöllhorn, *Chem. Ber.*, **99**, 3108 (1966).

(3) The nomenclature of the imines with which we are concerned has not developed systematically. A system based on analogy with the nomenclature of quinone imines and diimines is proposed, in which i (usually termed a "sulfoximine") is termed a "sulfone imine," and ii,



i



ii

a "sulfone diimine." The "quinone imine" terminology is broadly applicable to most semipolar S→N (or P→N) compounds one might imagine.

The term "sulfoximine" for the monoimine of a sulfone is unfortunate in that it may connote the sulfoxide oxidation state, and thus the structure >S→NH, which has been variously termed a "sulfinimine," "sulfilimine," or a "sulfimine." The latter term, which has been adopted by Appel,[4] seems simplest and least ambiguous.

(4) R. Appel, W. Büchner, and E. Guth, *Ann.*, **618**, 53 (1958); R. Appel and W. Büchner, *Chem. Ber.*, **95**, 855 (1962).

(5) The necessary chloramine was generated from gaseous chlorine and ammonia using a modified version of the Sisler generator [H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3906 (1954)].

(6) The dimethyl homolog was more difficult to isolate, and was obtained in 12–39% yields. The sulfone diimines were actually formed to the extent of *ca.* 60%.

(7) Appel[2] reported the isolation only of dimethyl sulfiminium chloride from dimethyl sulfide in acetonitrile. The diimine must have been formed but was liberated into the solvent as the free base.

(8) A recent paper [D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.*, **88**, 544 (1966)] suggests the possibility that the nitrile might have been formed by reaction of the olefin with NH, generated by thermal cleavage of an S→N bond. Neither olefin nor nitrile was found if the reaction was worked up by chromatography and the recrystallization step omitted.

(9) W. Theilacker and E. Wegner, *Angew. Chem.*, 72, 127 (1960).

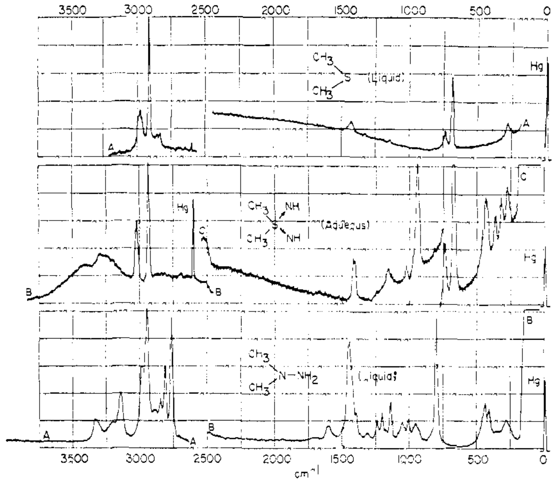


Figure 1. Raman spectra of dimethyl sulfide, aqueous dimethyl sulfone diimine, and unsymmetrical dimethylhydrazine. Gain: A, 100; B, 200; C, 500.

an intermediate, $R_2S^+(NH)Cl$, which is structurally analogous to sulfoxonium ions and which would solvolyze to the sulfone imine.

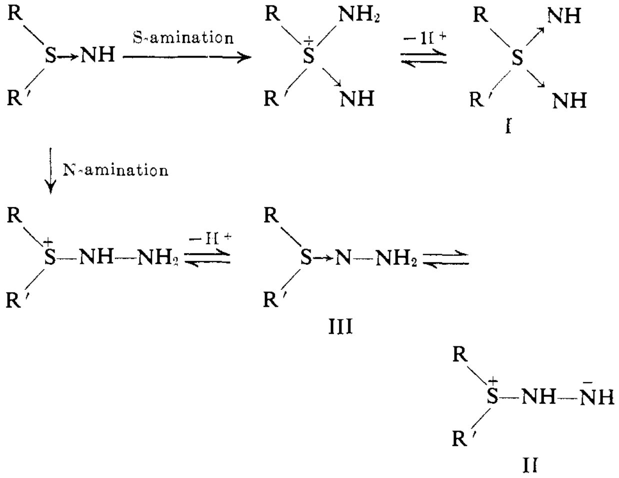
The sulfoxide could also conceivably have been formed by hydrolysis of the reactive sulfimine by adventitious moisture, although not by alcoholysis.[4] No alternate scheme for the formation of sulfone imine is apparent. The sulfone diimine is hydrolytically inert (see later), and the possibility that the sulfone imine could have been formed by amination of sulfoxide was also ruled out. The sulfoxide is nearly inert to chloramine under the reaction conditions, and it is inconceivable that the observed high sulfone imine:sulfoxide ratio (*ca.* 6:1) would have occurred if sulfoxide amination were the mode of sulfone imine formation.

It is clear from these results why hydroxylic solvents are to be avoided in the synthesis if possible. Displacement on chlorine likely occurs to some extent in acetonitrile; however, ammonolysis of the S-chloro species would lead to the same product as if direct displacement on nitrogen had occurred.[10]

Proof of Structure

The reported nmr spectra of the diimines formed from dimethyl and diethyl sulfide[1,2] clearly establish that the alkyl groups remain intact and exist in magnetically equivalent environments. The structural problem is reduced by these facts to determining whether the sulfimine intermediate is aminated by chloramine in the second stage of the synthesis on nitrogen or on sulfur. Amination on sulfur leads to structure I and tetrahedral coordination of sulfur, while N-amination yields II or III and trigonal sulfur. The dipolar form II would probably be much less stable than its tautomeric isomer III. Both tautomers have equivalent skeletal symmetry that is distinctly different from the tetrahedral diimine structure, I. Thus, the vibrational spectrum ought to allow one to distinguish between these two forms.

Here we report the Raman spectra of the dimethyl, diethyl, and methyl dodecyl derivatives of the chloramine–dialkyl sulfide reaction product. A vibrational



analysis and band assignment for the dimethyl derivative is consistent with C_{2v} symmetry, and strongly supports I as the correct structure of the group. Additional evidence has been obtained from infrared spectra and from the chemical properties of the compounds. The latter evidence is considered later at appropriate points in the description of these properties.

Dimethyl Sulfone Diimine. A. Spectroscopic Evidence. The Raman spectrum of a concentrated aqueous solution of the dimethyl sulfone diimine is exhibited in Figure 1 along with comparison spectra of liquid dimethyl sulfide and unsymmetrical dimethylhydrazine (u-DMH). Qualitative inspection of the spectra indicates the preservation of bands arising from the $(CH_3)_2S$ functional group and the completely different pattern for the hydrazine spectrum. In particular, we note the absence of an intense, polarized band in the 700–900-cm^{-1} range which can be assigned as the N–N stretching region for a hydrazine structure (808 cm^{-1} (Raman), 802 cm^{-1} (infrared) for u-DMH). In addition, we can find no evidence for bands associated with the NH_2 group. In u-DMH, the $\delta(NH_2)$ deformation occurs at 1606 cm^{-1} with $2\delta(NH_2)$ at 3207 cm^{-1}, probably in Fermi resonance with $\nu_{sym}(NH)$ at 3332 cm^{-1}. These NH_2 motions persist as discernible features in 25% aqueous solutions of u-DMH. In chloroform solution, both the Raman and the infrared spectra of I exhibit a single band at 3311 cm^{-1}, indicating degeneracy of the in-phase and out-of-phase NH stretch consistent with $R_2S(NH)_2$ and not R_2S–N–NH_2.

Table I summarizes the Raman data obtained on the aqueous sample of dimethyl sulfone diimine. Frequency assignments are based on comparison with the Raman spectra of dimethyl sulfide ($(CH_3)_2S$)[11] and dimethyl sulfone ($(CH_3)_2SO_2$),[12] and the infrared data on sulfamide ($(NH_2)_2SO_2$).[13] For clarity, bands associated with the sulfonyl group or interaction of SO_2 with other modes have been omitted from the table.

The dimethyl sulfide group appears to be unperturbed by formation of the diimine structure though the methyl hydrogen stretches do appear to be sensitive to changes in sulfur bonding. Again, note the absence of bands associated with the NH_2 group: NH_2 rocking modes at 720 and 1131 cm^{-1}, the NH_2 scissors at 1557

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[10] H. Takei, I. Watanabe, and T. Makaiyama, *Bull. Chem. Soc. Japan*, **38**, 1989 (1965).

[11] The data tabulated here are in substantial agreement with that of R. Fonteyne, *J. Chem. Phys.*, **8**, 60 (1940).

[12] W. R. Feairheller, Jr., and J. E. Katon, *Spectrochim. Acta*, **20**, 1099 (1964).

[13] I. W. Herrick and E. L. Wagner, *ibid.*, **21**, 1569 (1965).

Table I. Raman Spectra of Dimethyl Sulfone Diimine and Comparison Compounds (cm^{-1})[a]

Aqueous[b] $(CH_3)_2S(NH)_2$	Liquid[b] $(CH_3)_2S$	Aqueous[c] $(CH_3)_2SO_2$	Infrared cryst[d] $(NH_2)_2SO_2$	Assignment
278 m	282 s	292 s		$\delta(SC_2)$, scissors
326 m		320 s		$r(SC_2)$, rock
371 m			362	$\delta(SN_2)$, scissors
			422	$\tau(SNH_2)$, NH_2 torsion
436 m			506	$r(SN_2)$, rock
460 w			486	$t(SN_2)$, twist
679 vs, P	691 vs, P	700 vs, P		$\nu_s(CS)$, sym stretch
			720	$r(NH_2)$, NH_2 rock
741 m	742 s	770 s		$\nu_{as}(CS)$, asym stretch
947 s, P			902	$\nu_s(SN)$, sym stretch
(975 vw)[e]			929	$\nu_{as}(SN)$, asym stretch
1162 w			1131	$r(NH_2)$, NH_2 rock
1026 w, P	1149 w	950 w		$r(CH_3)$, rock
	1221 w	1006 m, P		
	1266 w	1090 w		
1225 vw	1341 w	1292 w		
1408 m	1427 m	1407 s		$\delta(CH_3)$, bend
1420 m	1444 m	1430 ms		
			1557	$\delta(NH_2)$, NH_2 scissors
	2831 w			$2\delta(CH_3)$ (?)
	2853 w			
2932 vs, P	2914 vvs, P	2928 vs, P		$\nu_s(CH)$, sym stretch
	2968 s			
3018 s	2982 s	3024 vs		$\nu_{as}(CH)$, asym stretch
			3112	ν (NH), stretch
3250 m, B			3223	
			3323	

[a] Abbreviations used are: w, weak; m, medium; s, strong; v, very; P, polarized; B, broad. [b] This work. [c] Reference 12. [d] Reference 13. [e] Shoulder visible only with axial polarization.

Table II. Raman Spectra (cm^{-1})[a]

$(CH_3)_2S(NH)_2$ Solid	$(CH_3)_2S(O)NH$ Solid	50% aqueous	Assignment
274 w	285 m	285 s	$\delta(SC_2)$, scissors
325 m	315 m	319 s	$r(SC_2)$, rock
368 w	374 w	373 m	$\delta(SN_2, SNO)$, scissors
435 s	466 s	457 s	$r(SN_2, SNO)$, rock
452 w	442 m		$t(C_2–S–N_2)$, twist
685 vs	694 vs	690 vs, P	$\nu_s(CS)$, sym stretch
746 m	762 m	762 s	$\nu_{as}(CS)$, asym stretch
	814 w		?
		934 w	$r(CH_3)$, rock ?
918 s	971 m		$\nu_s(SN)$, stretch
933 s	989 w	989 s, P	(crystal splitting ?)
962 vw			$\nu_{as}(SN)$, asym stretch
1006 vw			
	1031 w	1050 m, P	$\nu(SO)$, stretch
1161 w	1122 w		$\delta(SNH)$, bend ?
	1150 w	1132 w, P	
	1212 w	1206 w	$r(CH_3)$, rock
1405 w	1403 m	1406 m	$\delta(CH_3)$, bend
1418 w	1434 m	1423 m	
2930 vs	2925 s	2933 s, P	$\nu_s(CH)$, sym stretch
3015 s	3009 m	3019 s	$\nu_{as}(CH)$, asym stretch
3190 m	3191 w	3274 m, B	$\nu(NH)$, stretch
		3410 m, B	$\nu(OH)$, water band

[a] Abbreviations used are: w, weak, m, medium; s, strong; v, very; P, polarized; B, broad.

cm^{-1}, and the NH_2 stretch triplet at 3112, 3223, and 3323 cm^{-1} in the sulfamide.

The Raman spectrum of crystalline $(CH_3)_2S(NH)_2$ and of a 50% aqueous solution of dimethyl sulfone imine ($(CH_3)_2S(O)NH$) are presented in Figure 2. Table II summarizes the observed positions of the vibrations and proposed assignments. The similarity in the skeletal vibrations for these two molecules is immediately apparent. Not only is the visual display (pattern) of the spectra of these two tetrahedral molecules quite similar, but there are, in addition, many close coincidences in the actual positions of bands arising from similar modes of vibration. The replacement of NH by O transforms the weak $\nu_{asym}(SN)$ at 962 cm^{-1} into the more intense $\nu(SO)$ at 1031 cm^{-1} (1050 cm^{-1} in aqueous media).

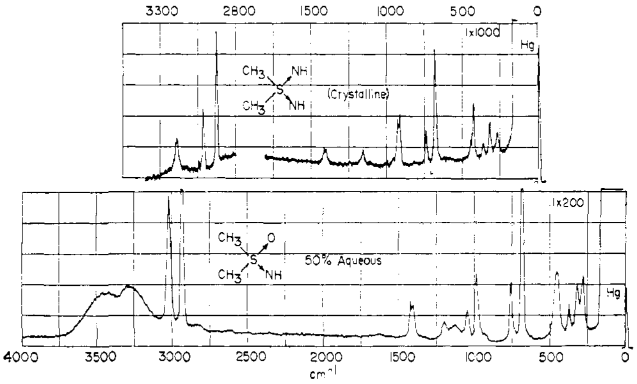

Figure 2. Raman spectra of crystalline dimethyl sulfone diimine and aqueous dimethyl sulfone imine.

B. Vibrational Assignment. The dimethyl sulfide reaction product can be analyzed as a pseudo-pentatomic molecule if we neglect all hydrogen motions. This is a reasonable approximation since we expect only very weak coupling between the light hydrogen atom vibrations and motions of the heavier skeletal atoms. For each of the pentatomic models we expect nine fundamental skeletal vibrations with all modes observable

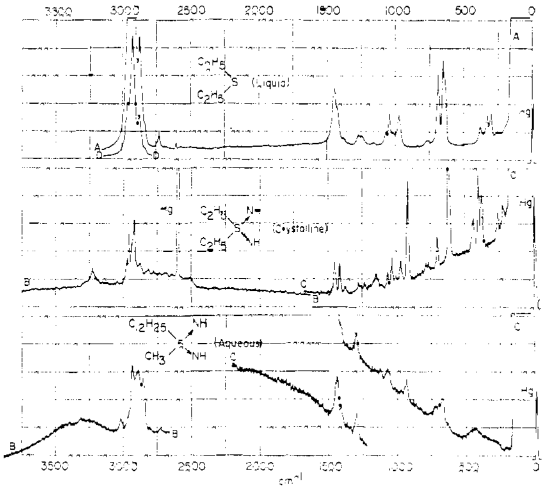

Figure 3. Raman spectra of diethyl sulfide, crystalline diethyl sulfone diimine, and methyl dodecyl sulfone diimine. Gain: A, 100; B, 200; C, 500; D, 40.

in the Raman. Four of these fundamentals should arise primarily from stretching motions and five from angle deformations.

The diimine structure I has C_{2v} symmetry. Its vibrational representation is $4A_1 + A_2 + 2B_1 + 2B_2$. There should be one inactive infrared fundamental (A_2, a torsional mode) and four polarized Raman lines. Two of the latter should be intense and arise from C–S and N–S stretching motions.

The hydrazine structure III (or II) has C_s molecular symmetry. With a vibrational representation of $6A' + 3A''$, all modes should be active in both the infrared and Raman. However, the six A' modes should be polarized in the Raman and three of these should be strong lines related to C–S, S–N, and N–N stretching motions.

Since hydrogen deformations are weak scatterers in the Raman, we can expect all strong bands observed below 1100 cm^{-1} to arise from skeletal motions. The Raman spectrum of an aqueous solution of the alkyl sulfide reaction product exhibits only two strong polarized lines in the skeletal stretching region and no evidence for a third, strong, polarized band associated with the N–N stretch. We associate the paired couplets 679, 741, and 947, 975 cm^{-1} with the symmetric and asymmetric motions of $(CH_3)_2S$ and $(NH)_2S$, respectively, and note the absence of strong interaction between the two pairs of vibrators. The remaining five bands we assign to the predicted five deformation modes. The proposed band assignments for the skeletal motions are summarized in Table III. The assignment of ν_7 and ν_9 to SNH motions is based on the increase in apparent intensity of the respective Raman bands upon crystallization and the formation of intermolecular hydrogen bonds (see below). All assignments are consistent with those of ref 12 and 13.

Dialkyl Sulfone Diimines. In addition to the methyl derivative, we have also examined the Raman spectra of the diethyl and the methyl dodecyl derivatives. Representative data are listed in Table IV with typical spectra illustrated in Figure 3. Spectral assignments are complicated by the presence of rotational isomers[14] which generate multiple strong Raman bands in the 600–700-cm^{-1} region. Diethyl sulfide data have been included to aid in the comparison. Again we note the persistence of the characteristic vibrations of the dialkyl sulfide group and the absence of strong perturbation by amination. These data are also quite consistent with the diimine structure proposed for the dimethyl sulfide reaction product. The characteristic positions for Raman bands associated with the $S(NH)_2$ structural unit in dialkyl sulfone diimines are summarized in Table V. The variation in characteristic frequency appears to be consistent with the effects of hydrogen bonding on each vibrational mode and the presence of water in the sample. The S–N asymmetric stretch and the SNH deformation would be expected to be more prominent in the infrared, and may be of some diagnostic value.

Table III. Symmetry Assignment for $(CH_3)_2S(NH)_2$

—Symmetry— Class	Specie	Frequency,[a] cm^{-1}	Approximate mode description
A_1	ν_1	947	S–N symmetric stretch
	ν_2	679	C–S symmetric stretch
	ν_3	371	NSN bend
	ν_4	278	CSC bend
A_2	ν_5	460	Torsion, $S(NH)_2$ twist
B_1	ν_6	975	S–N antisymmetric stretch
	ν_7	436	$S(NH)_2$ rock $\perp$ $S(CH_3)_2$ plane
B_2	ν_8	741	C–S antisymmetric stretch
	ν_9	326	$S(NH)_2$ wag $\|\|$ $S(CH_3)_2$ plane

[a] Aqueous solution

Properties

Thermal Stability. The thermal stability of dimethyl and diethyl sulfone diimines is sufficient to allow them to be analyzed by gas chromatography at 150°, with partial decomposition at the inlet. After 16 hr at 100°, neat methyl dodecyl sulfone diimine is largely decomposed, to the products shown.

$$C_{12}H_{25}S(NH)_2CH_3 \xrightarrow[16\text{ hr}]{100^\circ} \begin{array}{ll} C_{12}H_{25}SCH_3 & (50\%) \\ C_{10}H_{21}CH{=}CH_2 & (30\%) \\ C_{11}H_{23}C{\equiv}N & (5\%) \\ \text{unknown} & (5\%) \end{array}$$

Ammonia, azide (N_3^-), and thiocyanate (SCN^-) were also detected.

As with amine oxides,[15] the thermal stability of the sulfone diimines is greatly enhanced in hydroxylic solvents. An aqueous solution of methyl dodecyl sulfone diimine underwent less than 10% decomposition under the same conditions which completely decomposed the neat sample (above).

Hydrolysis and Reduction Reactions. The extraordinary resistance of sulfone diimines toward acid- or base-catalyzed hydrolysis[2] has been confirmed. Dimethyl sulfone diimine was recovered unchanged after 67 hr at 100° in water; no hydrolysis products were detectable either by infrared spectra or gas chromatographic analysis. Similar results were obtained after 1.5 hr at 100° in 2 *N* sodium hydroxide.

The cleavage of the C–S bond in sulfone diimines by aqueous hydrochloric acid to form alkyl chlorides and sulfinic acids has been reported,[2] and we obtained

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(14) D. W. Scott, J. P. McCullough, *et al.*, *J. Am. Chem. Soc.*, **74**, 4656 (1952) (cites unpublished work of J. R Nielsen, on diethyl sulfides).

(15) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

Table IV. Raman Spectra (cm^{-1})[a]

$(CH_3CH_2)_2S$[b]	$(CH_3CH_2)_2S(NH)_2$		$(C_{12}H_{25})(CH_3)S(NH)_2$		Qualitative description
Liquid	Crystal	Aqueous	Crystal	Aqueous	
187 w	227 w				CSC skeletal bend
256 vw	267 w	260 vw			
305 m, P		313 w	306 w	303 w	Skeletal deformations
334 m, P		343 m			
383 w	382 m		376 w	356 w	
	407 s	407 m	417 vw		
	444 m	444 w	445 vw	437 m	SN_2 rock
		475 w	470 vw		
		521 w	510 vw		
		621 s	610 vw		C_2S sym stretch (rotational isomers)
639 vs, P	619 s	636 vs, P		643 w, P	
657 vs, P		662 m, P		683 s, P	
693 s	707 w	700 m	707 s	707 m, P	
764 vw	774 vw	779 vw	734 m	732 m, P	C_2S asym stretch
778 vw	792 vw	817 vw	817 w		
	922 s	945 s, P	925 m	943 m, P	S–N sym stretch
975 s	976 w	979 w	957 w	979 w, P	C–C sym stretch
1017 w	1010 vw	1026 w			Combination?
1047 s	1043 w	1041 w	1056 w	1071 w	CH_2 deformation
1074 m	1068 w	1074 w	1083 w	1084 w	
	1155 w, B	1150 w, B	1125 m	1131 w	SNH bend?
			1167 vw	1165 vw	
1249 w	1238 vw	1236 w	1207 vw		Overtone?
1274 w, P	1282 vw		1295 m	1306 s	
1382 w	1380 vw	1382 w			
1427 s	1421 w	1414 m	1412 w	1418 m	CH_2 deformation
1450 s	1456 w	1456 m	1442 m	1444 s	
			1458 m		
2729 m, P					CH stretch
2874 s, P	2877 w	2885 s	2850 vs	2857 vs, P	
	2922 vs		2879 vs	2895 vs, P	
2929 vs, P	2937 m	2939 vs	2928 vs	2934 vs, P	
2966 s	2959 m				
	2976 w	2988 s		3018 m	
	3227 w	3290 s, B	3180 w		NH stretch
			3222 w		
			3307 w	3304 m, B	
				3397 m, B	H_2O stretch

[a] Abbreviations used are: w, weak; m, medium; s, strong; v, very; P, polarized; B, broad. [b] Data below 1500 cm^{-1} from ref 14.

Table V. Characteristic $R_2S(NH)_2$ Raman Bands

Type of motion	Position, cm^{-1}	Quality
SN_2 deformation	340–380	m, P
SN_2 rock	435–445	m
S–N sym stretch	920–950	s, P
S–N asym stretch	960–980	w
SNH deformation	1125–1160	w
NH stretch	3190–3335	m

Table VI. Acid Dissociation Constants of Protonated Sulfone Diimines and Other Compounds

Compound	pK_A
$(CH_3)_2S(NH)NH_2^+, Cl^-$	5.59 ± 0.01[a]
$(C_2H_5)_2S(NH)NH_2^+, Cl^-$	5.93 ± 0.05[a]
$C_{12}H_{25}(CH_3)S(NH)NH_2^+, Cl^-$	4.73 ± 0.1[a]
$(CH_3)_2S(O)NH_2^+, Cl^-$	3.24 ± 0.02[b]
$(CH_3)_2S^+(O)OH, Cl^-$	-12.3[c]
$(CH_3)_2S^+OH, Cl^-$	0[d]
$(CH_3)_3NOH^+, Cl^-$	4.65[d]

[a] Calculated from potentiometric titration curves following the method of A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p 33. [b] Calculated following the method of Albert and Serjeant, p 38. [c] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42,** 1113 (1964). [d] P. Nylen, *Z. Anorg. Allgem. Chem.*, **246,** 227 (1941).

identical results. Unexpectedly, the reaction took a completely different course in aqueous hydrochloric acid containing potassium iodide (2.4 *N* HCl, 6 *N* KI). A few per cent cleavage to alkyl halides was again observed, but the major products were the dialkyl sulfide and iodine. Sulfoxides are also reduced to sulfides by iodide in acidic solution.[16]

The reluctance of the group to undergo acid- or base-catalyzed hydrolysis to sulfone imines or sulfones constituted supporting evidence for structure I. The related sulfone imines are also resistant to hydrolysis, whereas structures II or III, being N-substituted sulfimines, should resemble the parent sulfimines in being readily hydrolyzable.

Methyl dodecyl sulfone diimine reacted exothermically with massive quantities of hydrogen-bearing W-2 Raney nickel in alcohol. Methyl dodecyl sulfide (18%) and dodecane (10%) were isolated.

Basicity and Metal Complexing. The pK_A data in Table VI show that the sulfone diimines are weakly basic molecules. They are about 2.5 pK units more basic than sulfone imines.

The pK_a data also constitute evidence which favors I as the correct structure of the group. Structure III can be viewed as a modified hydrazine, in which a partial negative charge resides on one nitrogen.

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(16) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Letters*, 2691 (1964).

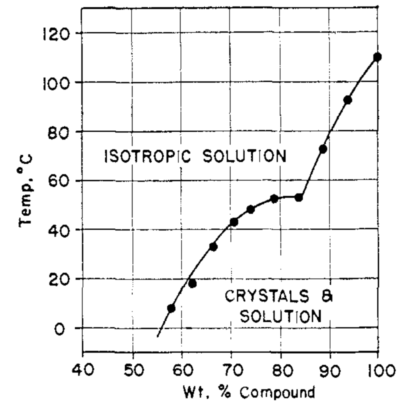
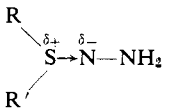


Figure 4. Solubility diagram of dimethyl sulfone diimine in water.



III

This negative charge would be expected to increase the basicity of III over that of hydrazine itself, so that the predicted pK_A of the conjugate acid of III should be >8.5. The much lower values observed rule against structure III. It is impossible to predict exactly what the basicity of I should be, but if the same difference exists between its basicity and that of NH_2^- as exists between that of sulfones and OH^-, a value in the neighborhood of 6 for the pK_A of its conjugate acid would be anticipated.[17] The original structure proposal,[1] R_2S^+–NH–NH^-, is not stabilized by semipolar bonds and, in having an amide ion insulated from the sulfur by the –NH– group, should be considerably more basic than was observed (compare $R_3N^+NH_2$ with a pK_A > 15).

The metal complexing ability of the sulfone diimine group with metal salts from vanadium to zinc in the first long row of the periodic table (in convenient oxidation states) was screened in a qualitative fashion. Obvious complexing occurred only with V(IV), Cr(III), Fe(III), and Cu(II). The complexing ability of the sulfone diimine thus parallels that of aliphatic amine oxides in general, in line with the close similarity in basicity of the two groups (Table VI).

With silver nitrate, each of the sulfone diimines formed an insoluble grayish precipitate which was accompanied by a sharp decrease in the pH of the solution to 2–3.[18] It thus appears that actual liberation of mineral acids occurs in aqueous solution through reaction with silver ion, although potentiometric titration with base revealed no clean-cut stoichiometry. No such pH effect was noted with any other metal ion. Formation of the precipitate was reversible: addition of nitric acid redissolved it. Also, it was not formed from silver acetate in glacial acetic acid. The latter system constituted a convenient qualitative test for chloride in the presence of sulfone diimines.

Polarity and Hydrogen Bonding. The sulfone diimine group is a polar functional group, as indicated by the high water solubility of the dialkyl derivatives. Figure 4 describes the water solubility of dimethyl sulfone diimine. Methyl dodecyl sulfone diimine is likewise water soluble, while methyl dodecyl sulfone is by contrast totally insoluble.

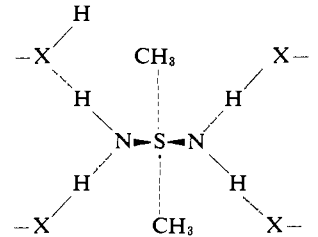
The vibrational spectral data suggest that the sulfone diimine group readily engages in hydrogen bonding. Spectrally, hydrogen-bond formation is manifested in intensity changes, band broadening, and frequency shifts.[19] For dimethyl sulfone diimine ν_7, ν_1, and ν(NH) are shifted from 415, 933, and 3311 cm^{-1} in relatively inert chloroform to 436, 947, and 3250[20] cm^{-1} in aqueous solution. This corresponds to an increase in the resistance to deformation of a bending mode and an effective elongation of the NH bond upon hydrogen bond formation. Dimethyl sulfone imine exhibits similar spectral effects in a comparison of chloroform and aqueous solution spectra: ν(SN) shifts from 982 to 989 cm^{-1}, ν(SO) from 1020 to 1050 cm^{-1}, and ν(NH) from 3340 to 3274 cm^{-1}.

Hydrogen-bond formation is more pronounced in the crystalline state, as indicated by the larger shift of the NH stretching frequencies summarized in Table VII. Extensive hydrogen bonding is evident in crystalline dimethyl sulfone diimine: ν_3 and ν_7 are stronger and sharper bands and ν_1 is split into two components. The splitting is interpreted as arising from intermolecular interaction rather than local site symmetry effects since ν_2 is not split in the crystalline spectrum.[21]

Table VII. NH Stretching Bands, cm^{-1}

Compound	Crystal	Aqueous	$CHCl_3$
$(CH_3)_2S(NH)_2$	3190	3250	3311
$(CH_3)_2S(O)NH$	3191	3274	3340
$(C_2H_5)_2S(NH)_2$	3227	3290	. . .
$(CH_3)(C_{12}H_{25})S(NH)_2$	3178 3222	3304	. . .

Only one type of imine hydrogen is indicated in the solution and crystalline spectrum for the dimethyl derivative; thus we propose a general structural model of the form



X = O, N

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[17] The pK_A of H–OH (15) is lowered to −12 in $R_2S^+(O)$–OH, a difference of 27 pK units. Taking 33 as the pK_A of NH_3, $R_2S^+(O)NH_2$ should have a value of 6 if the same difference were observed (the actual value is 3), and $R_2S(NH)$–NH_2 would not be expected to be terribly different. This crude line of reasoning only shows that the observed values are in a resonable range.

[18] The formation of a precipitate with silver ion was previously reported,[2] but not the pH effect.

[19] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

[20] All aqueous NH stretching bands are broadened and their positions are less certain owing to variation in internuclear distance caused by hydrogen bonding.

[21] Preliminary X-ray diffraction studies[22] indicate each of the eight molecules in the unit cell is situated at a local site with C_2 symmetry. Thus, ν_1 and ν_2 should be similarly affected if crystal site splitting is operative.

[22] N. Webb, these laboratories, personal communication.

to represent the spatial interaction with either water (aqueous) or diimine (crystal). This model also reflects the dual nature of the diimines in accepting and donating hydrogens in interaction with other electronegative atoms.

The shift of ν(NH) for crystalline diethyl sulfone diimine is 35 cm^{-1} less than for the dimethyl derivative, indicating a weaker hydrogen bond. This probably arises from van der Waals repulsion of the alkyl fragments leading to lattice packing problems. When one of the alkyl groups is replaced by a bulky long chain in the unsymmetrical methyl dodecyl derivative we observed two NH bands, indicating both a long and a short $NH\cdots N$ bond.

If we assume a value of 3350 cm^{-1} for free imine NH stretching frequency,[23,24] then the average shift of 160 cm^{-1} allows us to estimate the crystalline hydrogen-bond strengths for these diimines as 2.5–3.0 kcal/mole for an $NH\cdots\cdot N$ bond.[19,25,26] On the same basis, the interaction with water is probably of the order of 2.0–2.5 kcal/mole. Thus the solvation of the diimines is enhanced by the availability of 4–5 kcal/mole of diimine–water interaction energy.

Discussion

With the synthesis of the sulfone diimines, all the possible imines of sulfoxides[4] and sulfones have been studied. It is, therefore, of interest to compare the imines with each other and with the parent oxygen compounds.

The various imines may be conveniently divided into two classes: sulfoxide-like structures incorporating only one semipolar bond, and sulfone-like structures in which two semipolar bonds are formed to the same heteroatom. Comparison of the sulfone diimines with the sulfimines reveals that the same fundamental relationships in properties which exist between sulfones and sulfoxides also exist between the two classes of imines. The thermal stability of the sulfone diimines clearly exceeds that of the sulfimines. For comparable decomposition rates, roughly 100° higher temperatures are required of the sulfone diimines. Also, the basicity of the sulfimines appears to exceed that of the sulfone diimines, as is the case with sulfoxides and sulfones (Table VI). While direct measurement of the basicity of sulfimines in aqueous solution is precluded by their hydrolytic instability, they are known to form an adduct with carbon dioxide in nonhydroxylic solvents, $R_2S \rightarrow N^+HCO_2^-$,[27] whereas the sulfone diimine group does not. A chloroform solution of the latter saturated with carbon dioxide shows the free CO_2 infrared band, but no absorption corresponding to $-CO_2^-$ or $-CO_2H$. On the other hand, the sulfimines are not sufficiently basic to prevent their liberation from their conjugate acid, at least in part, by ammonia. The aqueous pK_A of the species $R_2S^+{-}NH_2$ is therefore most likely in the range 8–10.

Examination of the presently known imines reveals a striking difference between the two classes, above, with regard to hydrolytic reactivity. It appears to be generally true that sulfoxide-like imines are readily hydrolyzable to the parent oxygen compounds, while sulfone-like imines are hydrolytically inert. The acid- or base-catalyzed hydrolysis of a sulfone imine or diimine has so far never been observed.[28] Examples of hydrolytically reactive sulfoxide-like imines include $R_2S \rightarrow NH$[4] and $R{-}S(NH)NH_2$.[29] Similarly reactive phosphorus imines which are "sulfoxide-like" in the above sense include $R_3P \rightarrow NH$[30] and $(H_2N)_3P \rightarrow NH$.[31]

Now let us consider the relationship between sulfoxides and sulfones, and their imine derivatives. It is apparent that the thermal stability of the imines is significantly lower than that of the oxygen compounds. Sulfimines decompose at room temperature and below, sulfoxides in the vicinity of 150° and higher. Sulfone diimines decompose rapidly at slightly over 100°, sulfones only at temperatures well over 200°.[32] The sulfone monoimine is more like the sulfone than the sulfone diimine in this respect.

Another fundamental distinction between the S–N and S–O compounds is the course which thermal decomposition takes. Both fragment to olefins, when β elimination is permitted by the structure. However, the S–N compounds (both sulfimines and sulfone diimines) yield the parent dialkyl sulfide as a major decomposition product whereas with sulfoxides and sulfones the dialkyl sulfide is a very minor product.[33] The possibility that the dialkyl sulfide is not a primary decomposition product but is formed by a secondary reaction between olefin and mercaptan cannot be rigorously excluded.

Another prominent difference between the oxygen and nitrogen analogs exists with regard to basicity and metal complexing. The figures in Table VI indicate the two sulfone imines to be 15–18 pK units more basic than the corresponding sulfone, a figure comparable to the difference between amide and hydroxide ion (pK_A of $NH_3 \cong 33$, pK_A of $H_2O \cong 15$). The cause for the large difference in each case stems from the difference in nuclear charge of nitrogen and oxygen.

It is evident from this work that the sulfur atom of sulfimines is appreciably more nucleophilic toward chloramine than is that of sulfoxides. Chloramine reacts preferentially with the sulfimine intermediate in the presence of high ammonia concentrations at temperatures below 0°. Sulfoxides, by contrast, compete

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(23) A higher frequency than the 3311 cm^{-1} observed in $CHCl_3$ is expected since self-association and/or interaction with the acidic proton in chloroform would tend to lower the free =NH frequency.

(24) N. B. Colthup, *J. Opt. Soc. Am.*, 40, 397 (1950), cites a range of 3300–3400 cm^{-1} for an imine NH.

(25) R. Schroeder and E. R. Lippincott, *J. Phys. Chem.*, **61**, 921 (1957).

(26) D. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Am. Chem. Soc.*, 77, 6480 (1955).

(27) R. Appel and G. Büchler, *Ann.*, **684**, 112 (1965).

(28) Indirect hydrolysis of the monoimine by reaction with hydrogen peroxide or nitrous acid has been carried out [A. Schöberl and A. Wagner, "Methoden der Organischen Chemie (Houben-Weyl)," Vol. 9, Eugen Müller Ed., Georg Thieme Verlag, Stuttgart, 1955, p 220; F. Misani, T. W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, 73, 459 (1951)]. However, the monoimines have been recovered unchanged from refluxing 50% sodium hydroxide (J. S. Berry, private communication from these laboratories).

(29) This species is presumably formed as the initial sulfur-containing product of the hydrochloric acid cleavage of sulfone diimines. Hydrolytically reactive aromatic derivatives have also been reported [G. Kresse, C. Seyfried, and A. Trede, *Tetrahedron Letters*, 3933 (1965)].

(30) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, 81, 2982 (1959); R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).

(31) M. Becke-Goehring and K. Niedenzu, *ibid.*, 90, 2072 (1957).

(32) Methyl dodecyl sulfone distils with some decomposition at 355° at atmospheric pressure.

(33) Methyl dodecyl sulfoxide at 190–230° in an open system gave less than 1% sulfide. The yield of sulfide from pyrolysis of the sulfone was still less, if formed at all. See W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind.* (London), 342 (1966).

Table VIII. Melting Points and Analyses of Dialkyl Sulfone Diimines, RR′S(NH)$_2$

			% C		% H		% S		% N	
R	R′	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	CH_3	108.5-110	26.1	26.1	8.7	8.8	34.8	34.1	30.4	30.3
$C_{10}H_{21}$	CH_3	56-57	60.5	60.1	12.1	11.7	14.8	15.1	12.9	12.9
$C_{12}H_{25}$	CH_3	64.5-66.5	63.4	63.7	12.3	12.2	13.0	13.4	11.4	11.4
$C_{14}H_{29}$	CH_3	73.5-74.5	65.6	65.6	12.5	12.1	11.7	12.0	10.2	10.3
$C_{16}H_{33}$	CH_3	79-80	67.5	67.7	12.7	12.4	10.6	10.4	9.3	9.3

Table IX. Nmr Chemical Shifts of S-Methyl Groups (τ units)

	$CDCl_3$[a]	D_2O[b]
$(CH_3)_2S$	7.89	...
$(CH_3)_2SO$	7.39	...
$(CH_3)_2SO_2$	7.08	...
$(CH_3)_2S(O)NH$	6.90	...
$(CH_3)_2S(NH)_2$	6.94	6.59
$(CH_3)_2S^+(NH)NH_2, Cl^-$	6.36	6.10
$(CH_3)_2S^+(O)NH_2, Cl^-$	6.23	5.98[c]
$C_{12}H_{25}SCH_3$	7.94	...
$C_{12}H_{25}SOCH_3$	7.44	...
$C_{12}H_{25}S(NH)_2CH_3$	7.02	6.73
$C_{12}H_{25}S(O)(NH)CH_3$	7.10	...
$C_{12}H_{25}SO_2CH_3$	7.15	...

[a] Internal tetramethylsilane reference. [b] Tetramethylsilane capillary reference. [c] In the presence of excess HCl.

Table X. Nmr Spectra of $(C_2H_5)_2S(NH)_2$ (τ units)

Solvent	$CH_3(3)$	$CH_2(4)$	NH(1)	*J*, cps
D_2O	8.42	6.60	5.00	7.4
$CDCl_3$	8.61	7.00	8.27 (broad)	7.4
CCl_4	8.70	7.17	8.49 (sharp)	7.7
CCl_4[a]	8.7	7.1	8.1	...

[a] Reference 1.

very poorly with ammonia for chloramine under comparable conditions.

Experimental Section

Melting point (capillary, Mel-Temp apparatus, uncorrected) and analytical data are listed in Table VIII. Elemental analyses were performed by our analytical department. Nmr data were determined with a Varian HA-100 spectrophotometer. The chemical shifts of S-methyl groups in various compounds are tabulated in Table IX. The spectra of the long-chain compounds included other features expected from the structure, namely a triplet for the $-CH_2-$ α to the sulfur downfield from the S-methyl absorption, characteristic long-chain absorption at τ 8.75 and 9.15 (methylene protons and terminal methyl protons), plus broad absorption slightly downfield from most of the methylene protons attributable to the β-methylene group. Table X gives complete nmr data for diethyl sulfone diimine in various solvents.

Raman spectra were obtained on the Cary 81 Raman spectrophotometer using 4358-A mercury excitation and capillary cells (0.2-cc capacity). The instrument was calibrated with respect to argon, neon, and helium emission lines from low-pressure discharge lamps, and all strong Raman bands are believed accurate to ± 2 cm^{-1}. The hygroscopic nature of the samples made it convenient to obtain spectra from aqueous solutions although crystalline and chloroform solution spectra were also obtained. All solutions were filtered through activated charcoal and 0.45-μ Millipore filters to minimize fluorescence and scattering from particulate matter. Polarization data were obtained in the conventional manner using Polaroid cylinders.

Good infrared spectra were difficult to obtain free from the interfering effects of absorbed moisture. The solution spectra reported were taken on a Perkin-Elmer 421 grating spectrometer.

Gas chromatography was carried out on a Model 700 F & M instrument, using a 10% Apiezon on polytetrafluoroethylene column. Partial decomposition of the dimethyl sulfone diimine in the inlet (kept $<170°$) prevented quantitative application of gc, but a standard mixture of dimethyl sulfone, sulfone imine, and sulfone diimine approached the expected peak area ratios at high sample levels (several milligrams). Relative retention times of dimethyl sulfone, sulfoxide, sulfone imine, and sulfone diimine were 1.0, 0.87, 1.53, and 1.90, respectively. At a column temperature of 135° (0.25-in. columns, 50 cc of He/min), the sulfone had a retention time of *ca.* 3 min.

The reference sulfone imines were prepared from sulfoxides and hydrazoic acid by the method of Whitehead and Bentley.[34] Thin layer chromatography (tlc) was carried out on standard silica gel G plates, developed with methanol except where otherwise noted. The spots were visualized by spraying with 25% sulfuric acid and charring.

Dimethyl Sulfone Diimine. In a 500-ml, three-necked flask equipped with a 10-mm diameter gas inlet tube, stirrer, and $-30°$ cold-finger condenser fitted with a drying tube were placed 6.2 g (0.10 mole) of dimethyl sulfide and 180 ml of acetonitrile (dried over 4A molecular sieves). Chloramine-ammonia from a generator operating at 10 mmoles/min of Cl_2 and 10:1 NH_3:Cl_2 ratio[5] was passed in at $-15°$ for 1 hr (*ca.* 0.4 mole), and the flask packed in a $-20°$ ice-salt bath and stirred overnight. The temperature was 0° in the morning. The reaction was filtered, the filtrate evaporated to dryness *in vacuo*, and the residue sublimed at 80-90° (0.05 mm). Yields varied from 12 to 39% of material which was largely sulfone diimine contaminated by sulfoxide and sulfone imine according to gas chromatography. The hygroscopic crystals could be purified either by recrystallization from acetonitrile or resublimation. Attempts to improve this work-up procedure or scale up the reaction to 0.3 mole gave poorer yields.

Diethyl Sulfone Diimine. Diethyl sulfide (9.0 g, 0.10 mole) was aminated as described above for dimethyl sulfide. The filtrate was evaporated, taken up in acetonitrile, and washed with 50% aqueous potassium carbonate until chloride free (see preparation of methyl dodecyl homolog for description of test), the solvent evaporated, and the residue distilled; bp 70° (0.1 mm). The distillate (6.1 g, 51%) had a freezing temperature of 48°,[1,2] and was identical in both its nmr and infrared spectra with the compound synthesized by Cogliano and Braude. It could be gas chromatographed at 150° through the same column used for the dimethyl homolog.

Methyl Dodecyl Sulfone Diimine. In a 2-l. apparatus similar to that described above, but without the condenser, were placed 86.4 g (0.400 mole) of methyl dodecyl sulfide and 1300 ml of acetonitrile (dried over 4A molecular sieves). Chloramine was passed into the flask at 0-5° during four 1-hr periods, at an average rate of 0.40 mole/hr. After each 1-hr period, the glass wool-ammonium chloride filter was replaced. The reaction was then stirred overnight at 0° and filtered cold.

The filter cake was extracted thoroughly with 2-propanol, and the bulk of the 2-propanol removed *in vacuo* using a rotary evaporator.[35] The residue was then redissolved in 2-propanol and washed several times with 50% aqueous potassium carbonate, until a test sample of *ca.* 1 ml, dissolved in 3-5 ml of glacial acetic acid, gave no precipitate with a few drops of aqueous 0.5% silver acetate test reagent. The 2-propanol was again evaporated and the solid residue recrystallized from ethyl acetate or acetonitrile, yield *ca.* 45%. Tlc indicated the once recrystallized product to be relatively pure but contaminated with sulfone imine, sulfoxide, and a material with R_f 0. Multiple recrystallizations reduced these impurities to a level not detectable on the chromatogram with a 1000-μg sample (<0.5%). Work-up of the mother liquors from recrystallization of the main product yielded 11% recovered sulfide, plus 12% 1-dodecene and 1% dodecanenitrile. Each was unambiguously identified by gas chromatography retention times on a polar and nonpolar column, infrared spectra, and (in the case of the nitrile)

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(34) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952).

(35) If this evaporation was omitted, it proved to be essentially impossible to wash the system free of chloride with the potassium carbonate.

the nmr spectrum. The sulfone diimine (Infracord, mull) showed infrared bands at 3.02 (m), 3.4 (s), 3.5 (s), 3.85 (m), 7.1 (m), 7.65 (m), 9.1 (s, broad), 9.5 (s), 9.75 (m), 10.15 (m), 10.45 (m), 10.85 (s), 13.1 (w), 13.45 (m), 13.55 (m), 13.9 (m), and 14.2 μ (w).

A similar preparation was carried out in molecular sieve dried 2-propanol. After stirring overnight, the reaction was filtered and the ammonium chloride precipitate washed with 2-propanol. The combined filtrate and washings were evaporated, taken up in 2-propanol, and worked up as described above; yield 44%.

Tlc of the crude 2-propanol reaction product after the carbonate washes showed four spots at R_f 0, 0.48, 0.64, and 0.75, which corresponded to an unknown compound (possibly the sulfimine or its hydrochloride, or the hydrochloride of the sulfone diimine), the sulfone diimine, the sulfone imine and/or sulfoxide, and the sulfide, respectively. To determine the amounts of these quantitatively, the amination was repeated under identical conditions on 2.00 g of sulfide, and the entire reaction product chromatographed on a silica gel column (22 × 280 mm), eluting first with 2-propanol and then with 3A ethanol. The yield of recovered sulfide (free of dodecene) was 8%, the sulfone imine–sulfoxide fraction 7%, and the sulfone diimine fraction 64%. The nmr spectrum of the sulfone imine–sulfoxide fraction showed the two components to be present in *ca.* 5:1 ratio, from the relative intensities of the S-CH_3 peaks at τ 7.05 and 7.46. A ratio of this magnitude was confirmed by tlc using a solvent system later found to resolve sulfoxide from sulfone imine (95:9:1:0.5 chloroform–methanol–water–acetic acid).

Methyl Decyl Sulfone Diimine. This compound was prepared from 0.3 mole of methyl decyl sulfide and 1.2 moles of chloramine in acetonitrile following the same procedure described above for the dodecyl homolog. The compound was isolated in 45% yield.

Methyl Tetradecyl (and Hexadecyl) Sulfone Diimine. These homologs could not be obtained in satisfactory yield in acetonitrile reaction medium, because the sulfide starting material crystallized from acetonitrile solution at the desired reaction temperature. They were, therefore, prepared in 2-propanol, in which the sulfides are more soluble in the cold. Tlc showed, however, that recrystallization failed to remove the sulfone imine impurity. It was necessary to resort to column chromatography on silica gel (described above) for purification.

Thermal Decomposition and Hydrolysis Experiments. These were carried out in sealed tubes immersed in a steam bath. In the case of the dimethyl homologs, the products were isolated by adding the reaction mixture to several volumes of 50% potassium carbonate and extracting with 2-propanol. It was shown that dimethyl sulfoxide, sulfone, sulfone imine, and sulfone diimine could all be recovered from aqueous solution in high yield by this technique. In 2 *N* acid, no recoverable products were found after 30 min at 100°. Decomposition products of the dodecyl compound in acid were unambiguously identified by comparison of gas chromatography retention times and infrared spectral data with those of authentic materials. Yields, where reported in the text, were determined by injecting several large samples (30–40 μl) in the gc and weighing the fractions collected.

Decomposition experiments on the dodecyl homolog in 2.4 *N* HCl–6 *M* KI at 100° for 30 min gave I_2 (1.2 moles/mole of diimine) and a liquid which was principally methyl dodecyl sulfide (48%) containing dodecyl chloride and dodecyl iodide (combined yield 3%). However, when methyl dodecyl sulfone diimine was heated with 2 *N* HCl and worked up with a carbonate wash, a water-soluble long-chain potassium salt lacking an S–CH_3 in the nmr was isolated, in addition to dodecyl chloride, and was shown to be potassium dodecanesulfinate by reaction in aqueous solution with methyl iodide. Methyl dodecyl sulfone, identified unambiguously by infrared spectra and gas chromatography retention time, was isolated. The experiment was repeated, and the dodecyl chloride and dodecanesulfinic acid yields were estimated to be 53 and 37%, respectively.

No dodecyl mercaptan was ever detected among the decomposition products (gas chromatography)

Metal Complexing. Solutions (0.1 *M*) of dimethyl sulfone diimine, trimethylamine oxide, or trimethylphosphine oxide solutions were mixed with an equal volume of 0.1 *M* solutions of the metal salts. The phosphine oxide caused no visible change with any salt but $VOSO_4$ (blue → green). The visible changes with diimine and amine oxide were indistinguishable: $VOSO_4$, blue → green, gray precipitate; $Cr(NO_3)_3$, blue → green; $MnCl_2$, no change; $FeCl_3$, yellow → red-orange, prevented precipitation on standing which occurred in the control solution; $CoCl_2$, no change; $NiCl_2$, no change; $CuSO_4$, blue-green precipitate, identified as $Cu_4SO_4(OH)_6$ by the X-ray powder pattern; $ZnCl_2$, no change. Adding $CuSO_4$ solutions to a concentrated solution of the sulfone diimine gave an obvious deepening of the blue color.

Addition of $AgNO_3$ test reagent to any of the sulfone diimines in aqueous solution gave a gray precipitate, and a decrease in pH of the solution from *ca.* 8 to *ca.* 2.5. The precipitate did not form when the chloride test described above was used. Potentiometric titration with KOH of a system containing $AgNO_3$ and $(CH_3)_2S(NH)_2$ in 2.48:1 mole ratio gave a gradually sloping curve. The pH at 1 mole of KOH per mole of diimine was 4.8, and at 1.5 moles of KOH per mole of diimine was 6.8. Neither a precipitate nor a pH lowering was observed when dimethyl sulfone imine was mixed with $AgNO_3$.

Solubility Curve. The solubility of dimethyl sulfone diimine (Figure 4) was described by determining the temperature at which crystals separated on cooling and dissolved on heating with synthetic mixtures. The separating phase below the discontinuity is probably a quarter-hydrate. Nitrogen analyses on a sample crystallized from water and dried by blowing nitrogen over the sample at room temperature (which, incidentally, slowly evaporates the compound itself) gave values of 29.0, 28.9, and 29.2%; calculated for $(CH_3)_2S(CH)_2 \cdot 0.25H_2O$, 29.0%. The separating phase above the discontinuity is presumed to be anhydrous crystals.

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