1-Benzoyl-2,2-di-n-propyl-hydrazine. Prepared by the method of Liberman, Grumbach, and Rist[10] (mole ratio of benzoylhydrazine: sodium ethoxide: *n*-propyl bromide = 1:2:2, reaction time, 10 hr.), the yield was 30%. When the mole ratio was increased to 1:2:6, and the reaction time to 18 hr., the yield was 70%. M.p. and reported[10] m.p. 100–101°. The infrared spectrum of a sample in a potassium bromide pellet showed two strong bands at 1535 cm.$^{-1}$ and 1653 cm.$^{-1}$, characteristic of a secondary amide.[19] A strong band characteristic of bonded N—H appeared at 3210 cm.$^{-1}$ 1-Benzoyl-2,2-dimethylhydrazine has similar bands at 1555, 1653, and 3250 cm.$^{-1}$

1-Benzoyl-2,2-di-*n*-propylhydrazine was recovered unchanged from 20 hr. of refluxing with a large excess of either *n*-propyl bromide or methyl iodide in ethanolic solution.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KENTUCKY]

Ultraviolet Spectra of *N*-Sulfinyl Amines. Influence of Structure and Solvent[1]

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The ultraviolet spectra of some *N*-sulfinylanilines have been determined in ether and in several alcohols. The effect of substituents on the spectra and on the reaction of *N*-sulfinylanilines with alcohol is discussed.

The ultraviolet absorption spectra of some aliphatic and aromatic *N*-sulfinyl amines in hexane and cyclohexane have been reported by Mangini and Leandri.[2]

The work reported here is concerned with the spectra of some of these compounds in ether and in alcohols. In the cases where we have measured the spectra of compounds reported by Mangini and Leandri we find that there is little difference, if any, between the spectra in ether and in cyclohexane. Our work in ether has been primarily concerned with studying steric effects of ring substituents in *N*-sulfinylaniline. Such work, together with the spectra in alcohol, is of value in interpreting the structure of the NSO group.

The aliphatic *N*-sulfinyl amines characteristically absorb at about 230–240 mμ. The aromatic derivatives have a first primary band[3] at about 314–330 mμ, and in addition have a second primary band at about 230–240 mμ. The exact position of the first primary band is influenced to a small extent by the nature and position of a single substituent on the aromatic ring.

We interpret the second primary band (at 230–240 mμ) as being due to the ordinary isolated NSO grouping. The first primary band (at 314–330 mμ) is apparently due to the overall conjugated system consisting of the NSO group and the aromatic ring.

To obtain evidence that the band at 313–330 mμ is due to the conjugation of the NSO group with the aromatic ring we have prepared 2,4-dimethyl-*N*-sulfinylaniline and 2,6-dimethyl-*N*-sulfinylaniline and have compared the spectra of these two compounds.

In order for the NSO group to be conjugated with the aromatic ring the sulfur and nitrogen must be coplanar with the ring. Molecular models show that there will be considerable interference between the NSO group of *N*-sulfinylaniline and methyl groups in the *ortho* position. A comparison of the spectra of 2,4-dimethyl-*N*-sulfinylaniline shows that the interference caused by two *ortho* methyls has a pronounced effect on the spectra. 2,4-dimethyl-*N*-sulfinylaniline has a log ε of 4.05 at 337 mμ. In the 2,6-isomer the first primary band at 337 mμ has shifted to shorter wave lengths and has decreased in intensity to such an extent (log ε 3.27) that it is apparent only as a shoulder at 285 mμ of the second primary band. This result is in agreement with the idea outlined above that the first primary band is due to the over-all system consisting of the aromatic ring and the NSO group.

A secondary band which is either absent or is fused with the first primary band in 2,4-dimethyl-*N*-sulfinylaniline is accentuated by the two *ortho* methyl groups and appears at 367 mμ, log ε 3.24.

The shift of the first primary band to longer wave lengths in 2-methyl-, 4-methyl-, and 2,4-dimethyl-*N*-sulfinylanilines appears to be related to the methyl substituents. Thus unsubstituted *N*-sulfinylaniline has a maximum at 314 mμ. The introduction of a methyl group in the 4-position shifts the maximum 14 mμ to 328 mμ. A 2-methyl substituent shifts the maximum 8 mμ to 322 mμ. In 2,4-dimethyl-*N*-sulfinylaniline the shift is 23 mμ. This is approximately equal to the

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-49. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) A. Mangini and G. Leandri, *Spectrochim. Acta,* **8,** 283 (1956). Also paper presented at XVIth International Congress of Pure and Applied Chemistry, Paris, July 1957.

(3) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.,* **69,** 2715 (1947).

sum of the shifts due to a 2-methyl and 4-methyl group.

A slight steric effect of a single *ortho* methyl group is seen in the decrease of log ϵ from 4.00 in *N*-sulfinylaniline to 3.98 in 2-methyl-*N*-sulfinylaniline. Even this slight decrease is significant here, since a methyl group in the *para* position causes an increase in log ϵ to 4.10.

The results with 4-bromo-*N*-sulfinylaniline and 2,4,6-tribromo-*N*-sulfinylaniline confirm the conclusions drawn from the methyl derivatives. The maximum at 325 mμ (log ϵ 4.07) for 4-bomo-*N*-sulfinylaniline is reduced to a shoulder at 318 mμ having a log ϵ of only 2.53 in the case of 2,4,6-tribromo-*N*-sulfinylaniline.

The literature contains conflicting reports as to the stability of *N*-sulfinyl amines in alcohol solvents. Michaelis[4] reported that *N*-sulfinylaniline could be distilled without decomposition from an absolute ethyl alcohol solution. Carré and Libermann[5] also reported that the *N*-sulfinyl amines which they investigated were soluble in absolute alcohol without decomposition. Carré and Libermann did report, however, that when *N*-sulfinylaniline was refluxed with *n*-butyl alcohol, the alcohol was dehydrated to unsaturated compounds which polymerized. Under vigorous conditions *N*-sulfinylaniline reportedly reacts with ethyl alcohol to give hydrogen sulfide. In view of these confusing reports, we have extended our study to include the ultraviolet absorption spectra of *N*-sulfinyl amines in alcohol solvents.

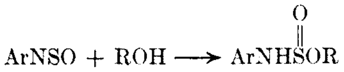
The spectra of both *N*-sulfinylaniline and *p*-nitro-*N*-sulfinylaniline have been determined in several alcohols. Since aniline shows a maximum at 285 mμ, compared to 314 for *N*-sulfinylaniline and *p*-nitroaniline has a maximum at 228, compared to 314 for *p*-nitro-*N*-sulfinylaniline it is possible to observe any disappearance of the NSO group by observing the wave length of maximal absorption. This wave length and the corresponding log ϵ value were taken as the criteria in determining whether any reaction had taken place. The extent of any reaction can also be estimated from the absorption data.

The spectrum of *N*-sulfinylaniline in absolute methyl alcohol is nearly identical with that of aniline in methyl alcohol, thus indicating rapid and complete reaction of *N*-sulfinylaniline with methyl alcohol. The spectrum in 2-chloroethanol indicates complete reaction in that solvent also. The spectrum of *N*-sulfinylaniline in ethanol shows no reaction in fresh solutions, but solutions on keeping for six days show a slow and eventually complete reaction.

N-Sulfinylaniline shows no reaction with allyl alcohol, ethylene glycol, isopropyl alcohol, *tert*-butyl alcohol, benzyl alcohol, and triethyl carbinol.

The spectrum of *p*-nitro-*N*-sulfinylaniline in each of the several solvents studied is similar to the spectrum of *p*-nitroaniline. The solvents used include methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *tert*-butyl alcohols and ethylene glycol. It is thus apparent that *p*-nitro-*N*-sulfinylaniline reacts with all of these alcohols.

The addition of alcohol to the NSO group might occur in the following way:



$$\mathrm{ArNSO} + \mathrm{ROH} \longrightarrow \mathrm{ArNH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{OR}$$

Such a reaction would destroy the conjugated system present in aromatic *N*-sulfinylamines and explain the observed change in the ultraviolet spectrum. An experiment with *N*-sulfinylaniline and methyl alcohol shows that the reaction goes further than shown above.

$$\mathrm{ArNHSO_2R} + \mathrm{ROH} \longrightarrow \mathrm{ArNH_2} + (\mathrm{RO})_2\mathrm{SO}$$

A 24% yield of dimethyl sulfite was obtained from methyl alcohol and *N*-sulfinylaniline in ethyl ether. The conditions used were almost certainly not optimum conditions. A much higher yield of dimethyl sulfite can be expected from this reaction when carried out under better conditions.

It will be recalled that the spectrum of *N*-sulfinylaniline in methyl alcohol indicated that one of the products was aniline. We have found that dimethyl sulfite exhibits a negligible absorption in the spectral region studied and would not show up as a product in the spectral study.

Earlier workers[6,7] have attempted to interpret the structure of the *N*-sulfinyl amino group on the basis of dipole moment studies. The structure Ar—N═S═O was found to fit the dipole moment measurements, but was ruled out because of the failure of *N*-sulfinyl amines to show any chemical

ULTRAVIOLET ABSORPTION OF AROMATIC *N*-SULFINYL AMINES[a]

	λ_1	log ϵ_1	λ_2	log ϵ_2	λ_3	log ϵ_3
N-Sulfinylaniline	231	3.78	314	4.00		
2-Methyl-*N*-sulfinylaniline	235	3.83	322	3.98		
4-Methyl-*N*-sulfinylaniline	238	3.75	328	4.11		
2,4-Dimethyl-*N*-sulfinylaniline	241	3.80	337	4.05		
2,6-Dimethyl-*N*-sulfinylaniline	235	3.78	285[b]	3.27	367	3.24
4-Bromo-*N*-sulfinylaniline	239	3.83	325	4.07		
2,4,5-Tribromo-*N*-sulfinylaniline	250[b]	3.45	318[b]	2.53	366	2.57
4-Nitro-*N*-sulfinylaniline	220[b]	4.00	314	4.12		

[a] Solvent is dry ethyl ether. [b] Shoulder.

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(5) P. Carré and D. Libermann, *Compt. rend.*, **194**, 2218 (1932).

(6) E. Bergmann and M. Tschudnowsky, *Z. Physikal. Chem.*, **17B**, 100 (1932).

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behavior similar to that of isocyanates. The reaction with alcohols which we have shown to take place is similar, at least in the first step, to the reaction of isocyanates with alcohols. The structure Ar—N=S=O must therefore be reconsidered as a possible structure for the N-sulfinyl amine group.

EXPERIMENTAL

The ultraviolet spectra were determined using either a Beckman DU spectrophotometer or a Beckman DK recording spectrophotometer. Solutions of the *N*-sulfinyl amines containing about 5 × 10^{-3} grams/liter were measured in 1 or 2 cm. silica absorption cells.

The following aliphatic *N*-sulfinyl amines have a single maximum as indicated: *n*-propyl- 234 mμ, $\log \epsilon$ 3.68; *n*-butyl- 234 mμ, $\log \epsilon$ 3.72; *n*-heptyl- 235 mμ, $\log \epsilon$ 3.67; cyclohexyl- 235 mμ, $\log \epsilon$ 3.83.

Isolation of dimethyl sulfite from N-sulfinylaniline and methyl alcohol. A mixture of 13.9 g. (0.10 mole) of *N*-sulfinylaniline, 9.6 g. (0.30 mole) of methyl alcohol, and 20 ml. of dry ether was allowed to stand at room temperature for 3 days. Distillation of the mixture gave 2.4 g. (24%) of dimethyl sulfite boiling at 122–123°.

Preparation of N-sulfinyl amines. These compounds were prepared in good yield following a procedure similar to that described by Michaelis.[4]

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Nitration of α-Oximino Esters and Acids[1]

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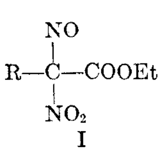
α-Oximino esters RC(=NOH)COOEt react with an equimolar mixture of 100% nitric acid and ammonium nitrate or with nitrogen dioxide in ether to give good yields of α-nitro-α-nitroso esters. The latter can be reconverted to α-oximino esters or oxidized to α,α-dinitro esters. The action of 100% nitric acid and ammonium nitrate upon other oximino esters, oximino acids, and related compounds has been investigated.

Oximino compounds have been utilized in various ways for the preparation of nitro compounds. A direct conversion of isonitroso to nitro groups can be accomplished by the oxidation of oximino compounds with sodium dichromate and sulfuric acid,[2] potassium permanganate,[3] hydrogen peroxide,[4] or peroxytrifluoroacetic acid.[5] The method of Iffland is less direct and involves bromination, oxidation, and debromination of oximes.[6]

Ketoximes react with nitrogen dioxide to yield pseudonitroles[7-11] which can be oxidized to *gem*-dinitro compounds with chromium trioxide in acetic acid,[7a] with nitric acid,[8] boiling ethanol,[10] or photochemically in benzene or ether.[8] In some cases the pseudonitroles are formed from ketoximes also by the action of fuming nitric acid,[10] and in a few instances the reaction with nitrogen dioxide[12,13] or nitric acid[13] will produce *gem*-dinitro compounds from ketoximes in one step.

In the present investigation α-oximino esters RC(=NOH)COOEt (R=alkyl) have been nitrated under various conditions. A mixture of 90% nitric acid and 15% fuming sulfuric acid at 5–15° gives products characterized by strong nitrate bands in the infrared (at 6.06, 7.86 ,and 11.74μ). Nitration with 100% nitric acid at 0–10° produces only small yields of mixtures containing nitrate esters which cannot be separated by molecular distillation. When the oximino esters are treated with an equimolar mixture of 100% nitric acid and ammonium nitrate, or with nitrogen dioxide in ether, insoluble blue oils, identified as α-nitro-α-nitroso esters (I), are formed in excellent yield.



$$R-\overset{NO}{\underset{NO_2}{C}}-COOEt$$

I

The new compounds (I, R = alkyl) are characterized by low-intensity absorption bands at 630-635 mμ. Their infrared spectra show two bands (NO, NO_2) in the 6.3μ region. They are sensitive to light, oxygen, heat, and prolonged exposure to

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(1) (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented before the Organic Section of the American Chemical Society at the 134th meeting, Chicago, September 1958.

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