Table V. Phenyl–Phenyl Contact Distances of *N,N′*-Diethyl-*N,N′*-diphenylurea (I) and *N,N′*-Dimethyl-*N,N′*-di(*p*-nitrophenyl)urea (II)

Atoms	I	II	
C(1)..C(1′)	2.89	2.81	0.08
C(1)..C(2′)	3.29	3.39	−0.10
C(1)..C(6′)	3.51	3.25	0.26
C(2)..C(2′)	4.10	3.85	0.25
C(2)..C(5′)	4.37	3.78	0.59
C(2)..C(6′)	3.46	3.37	0.09

seems to involve a partial dehybridization of the nitrogen atoms from the trigonal to the tetrahedral shape. This dehybridization is nearly the same for I and III, but a little less for II ($|\alpha - \beta| = 180°$ for a trigonal coordination of N). It is also accomplished by a rotation around the amide bonds which is almost the same for I and II and 10–15° larger for III. The other conformational parameters are quite normal. In Figures 4 and 5, projections of the structures of II and III, respectively, are reported; some of the shortest intermolecular contact distances are designated. As expected in both cases, the phenyl rings, with their polar NO_2 groups, face each other near symmetry centers at average distances of 3.4–3.6 Å.

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Registry No.—I, 85-98-3; II, 34594-47-3; III, 55676-48-7; nitric acid, 7697-37-2; *N,N′*-dimethyl-*N,N′*-diphenylurea, 611-92-7.

Supplementary Material Available. Tables of positional and thermal parameters and projections of structures II and III on [100] (3 pages). Ordering information is given on any current masthead page.

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N-Aryl-*S*,*S*-dimethyliminosulfuranes. Structure, Dipole Moments, and Extent of Double Bonding

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The crystal structure of *N*-(*p*-nitrophenyl)-*S*,*S*-dimethyliminosulfurane is reported. The short N–S bond (1.651 Å) implies a substantial amount of double bonding and bond length distortions in the aromatic ring suggest extensive resonance involvement of the *p*-nitrophenyl moiety. The dipole moments of five para-substituted *N*-aryl-*S*,*S*-dimethyliminosulfuranes (para substituents: F, Cl, Br, CN, NO_2) imply 45–58% ionic character in the N–S bond, least for *p*-F, most for *p*-NO_2. It is concluded that the two canonic forms $Ar{-}N^-{-}S^+Me_2 \leftrightarrow Ar{-}N{=}SMe_2$ contribute about equally to the resonance hybrid with the dipolar form predominating only when there are strongly electron-withdrawing substituents at the para position in the benzene ring.

The iminosulfuranes or sulfilimines, $X{-}N^-{-}S^+RR'$ or $X{-}N{=}SRR'$, constitute an interesting class of compounds because, like sulfoxides and sulfones, they exist in either zwitterionic structures or structures involving double bonds. The first representative of this type, *p*-$CH_3C_6H_4SO_2NSMe_2$, was synthesized in 1922;[2a] in this compound, the electron-withdrawing *p*-toluenesulfonyl group might be expected to stabilize the negative charge in the zwitterion. Five years later[2b] a similar compound but with the sulfur substituents $R = CH_3$ and $R' =$ *m*-$HOOCC_6H_4$ was resolved into optical antipodes, showing that the N–SRR′ moiety is pyramidal, and the conclusion was drawn that the compound must be zwitterionic since it was thought, at that time, that the N═S double-bonded form should be planar—an inference later recognized[3a] to be erroneous.

For over 45 years, with few exceptions,[4] the only iminosulfuranes known bore strongly electron-withdrawing substituents, usually sulfonyl or acetyl[5] groups, on the nitrogen. Investigation of the structure of these sulfonamido and acylamido compounds is due largely to a group of Hungarian investigators.[3,6–12] The N–SRR′ bond length in the *N*-sulfonyl derivatives is[7–9,12] 1.620–1.636 Å, considerably shorter than that (1.74 Å) calculated[7] from Pauling bond radii for an N–S single bond.[13a] It would thus appear that there is considerable N═S double bond character in iminosulfuranes,[13b] but as yet only an indirect estimate of 45% in *N*-tosyliminosulfuranes based on ESCA (x-ray photoelectron spectroscopy) data is available.[14] Qualitatively speaking, the acyl derivatives have longer N–S bond lengths (1.667–1.673 in $CCl_3CONSMe_2$ and $CHCl_2CONSEt_2$) than the sulfonyl analogues, presumably because the acyl group more effectively stabilizes the zwitterionic form, $R{-}C({-}O^-){=}N{-}S^+R_2$. Infrared studies[3b,6] of the N–S stretching frequency confirm decreasing N–S bond strength (and hence more $N^-{-}S^+$ and less N═S contribution) as X in XSO_2NSMe_2 becomes more electron withdrawing.

In 1968, the relatively stable *N*-aryliminosulfuranes became available[15] through the work of Claus and Vycudilik; additional syntheses of these compounds have since been reported by one of us as well as others.[16–19] We felt that a combination of x-ray structure analysis and dipole moment determination might throw light on the extent of polar bonding in these compounds.

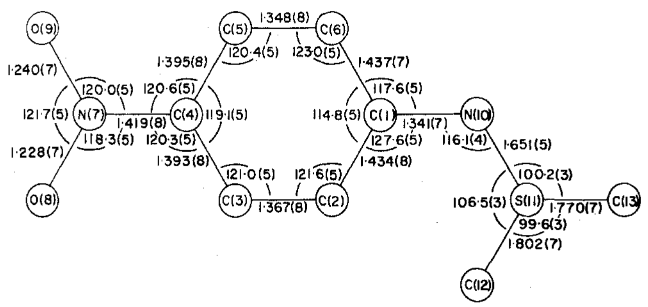
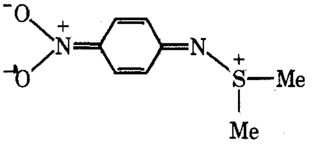


Figure 1. Bond lengths and bond angles in I. Estimated standard deviations in the last significant digit given in parentheses.

Results

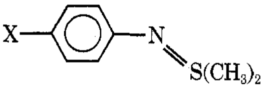
Structure Determination. The structure of *N*-(*p*-nitrophenyl)-*S*,*S*-dimethyliminosulfurane (I), determined by x-ray diffraction (heavy atom method), is shown in Figure 1. The $O_2NC_6H_4NS$– moiety is almost planar, the C(2)–C(1)–N(10)–S(11) torsion angle being −7°. One of the S–CH_3 groups is nearly in the same plane [torsion angle C(1)–N(10)–S(11)–C(13) = −164°] whereas the other *S*-methyl bond extends at right angles to that plane [torsion angle C(1)–N(10)–S(11)–C(12) = 92°]. The mean S–C bond length, 1.786 Å, is slightly shorter than the sum of Pauling's[20] single bond covalent radii, 1.81 Å, but lies close to the corresponding distances in *N*-(*p*-toluenesulfonyl)-*S*,*S*-dimethyliminosulfurane,[12] 1.798 Å, and the *N*-ethyl-*N*-(*p*-toluenesulfonyl)-*S*,*S*-pentamethyleneimoniumsulfurane cation,[13a] 1.789 Å. The slight difference between the two *S*-methyl bond lengths, 0.032 Å, may be significant, for although the methyl groups are enantiotopic in solution, they are diastereotopic in the crystal, as indicated above; it has been suggested in the literature[7] that this feature gives rise to differences in bond length.

The mean valency angle at the pyramidal sulfur atom, 102.1°, also agrees well with corresponding angles in analogous compounds which range[7–9,12] from 101.5 to 102.8°. The length of the N–S bond (1.651 Å) is intermediate between that in *N*-sulfonyl and *N*-acyliminosulfuranes (vide supra) suggesting an intermediate extent of covalent bonding. Presumably the resonance interaction of the aryl ring, which stabilizes the zwitterionic form and reduces double bonding, is intermediate between that of an *N*-acyl and that of an *N*-sulfonyl substituent:



The mean bond length in the benzene ring, 1.396 Å, is in excellent agreement with the normal value 1.394 (5) Å, but significant differences between the individual aromatic bond lengths reduce the regular benzene D_{6h} symmetry to C_{2v} with mean bond lengths C(1)–C(2), 1.435; C(2)–C(3), 1.358; C(3)–C(4), 1.394 Å. The endocyclic bond angles at C(1), 114.8°, and C(4), 119.1°, are also smaller than those at C(2,6), average 122.3°, and C(3,5), average 120.7°. Distortions of this type have been encountered previously[21–23] and a rationalization in terms of the amount of s character in each of the bonds has been advanced[24] to account for the observed geometries; a similar explanation appears to apply in the present case. The large difference between the exocyclic (C–C–N) angles (117.6, 127.6°) gives a measure of the valency angle deformations necessary to gain relief from nonbonded interactions between the ortho hydrogen at C(2) and the sulfur atom.

Table I. Observed and Calculated Dipole Moments for Para-Substituted *N*-Phenyl-*S*,*S*-dimethyliminosulfuranes



X	Dipole moment, D Found	Dipole moment, D Calcd[b]	Dipole moment, D Calcd[c]	μ_{NS},[a] D Calcd[d]
F	5.53	2.92	5.93	3.59
Cl	5.88	3.15	6.13	3.75
Br	6.11	3.15	6.13	4.01
CN	8.94	5.93	8.65	4.40
NO_2	10.1	6.98	9.63	4.63

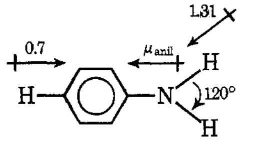
[a] Calculated; see text. [b] Assuming $\mu_{NS} = 0$; see text. [c] Assuming $\mu_{NS} = 4.04$ D; see text. [d] See text.

Dipole Moments. Dipole moments of sulfonyl derivatives of iminosulfuranes have been previously reported[25] but not interpreted. Dipole moments of the three *N*-chlorophenyl-*S*,*S*-dimethyliminosulfuranes have been measured[26] but the data given (1.56–1.81 D) are undoubtedly affected by a systematic error, being far too small, smaller, in fact, than the moments of the corresponding chloroanilines.

In the present work, the dipole moments of five para-substituted *N*-phenyl-*S*,*S*-dimethyliminosulfuranes were measured in benzene solution (in dioxane solution for I, which was insufficiently soluble in benzene) through determination of the variation in the dielectric constant of dilute solutions and use of the method of Higasi.[27] The results are shown in Table I, second column; the moments of this type of compound are obviously quite large, ranging from 5.5 to 10.1 D.

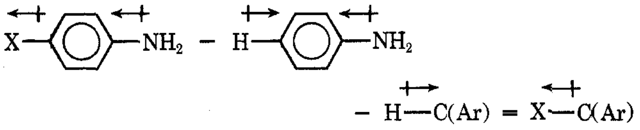
To calculate the bond dipole of the N^-–S^+ bond (Table I, last column) we first computed the expected dipole moments of the five iminosulfuranes studied assuming zero moment for the N–S bond (Table I, column 3). This was done on the basis of group or bond moments by a vector addition procedure. The bond moments taken from the literature[28] were ^+H–$C^-{}_{sp^2}$, 0.7 D; ^+C–$H^-{}_{sp^3}$, 0.4 D; ^+C–S^-, 1.6 D; ^+H–N^-, 1.31 D. The group moment μ_{anil} for *p*-C_6H_4N was calculated to be 0.95 D as shown in Scheme I, top. The Ar–X bond moments were computed from the literature dipole moments[29] of monosubstituted benzenes (NH_2, 1.56; F, 1.35; Cl, 1.58; Br, 1.57; CN, 3.93; NO_2, 3.93 D) and para-substituted anilines (F, 2.77; Cl, 3.01; Br, 3.01; CN, 5.85;[30] NO_2, 6.91 D) as shown in Scheme I, bottom, and are C(ar)–F, 0.51; C(ar)–Cl, 0.75; C(ar)–Br, 0.75; C(ar)–CN, 3.59; C(ar)–NO_2, 4.65 D; these values apply to para-substituted anilines and include the resonance interaction between the NH_2 group and the para substituent. The component moments along the three coordinate axes of the

Scheme I



$$\mu_{\text{aniline}} = 1.56 = 2 \times 1.31 \cos 60° + \mu_{\text{anil}} - 0.7$$

whence $\mu_{\text{anil}} = 0.95$ D



$$X\text{—}C_6H_4\text{—}NH_2 - H\text{—}C_6H_4\text{—}NH_2 - H\text{—}C(Ar) = X\text{—}C(Ar)$$

whence $\mu_{X\text{–}C(Ar)} = \mu_{p\text{-}XC_6H_4NH_2} - 2.26$ D

Table II. Component Dipole Moments (D) and Coordinates of N–S Vector

X	μ_x	μ_y	μ_z
F	0.520	−0.182	2.871
Cl, Br	0.625	−0.159	3.086
CN	1.869	0.115	5.624
NO_2	2.333	0.217	6.572
$(\vec{r})$	(0.76692	−0.58220	0.26996)[a]

[a] Coordinates of unit vector: r_x, r_y, r_z.

calculated moments given in Table I are shown in Table II; this table also has the coordinates of the unit vector describing the direction of the N–S bond which is needed in the sequel. The coordinates used in these computations are those given in Table VI (Appendix[31]) for the p-nitrophenyl compound; for the other four compounds, the NO_2 group moment was replaced by that of the appropriate substituent.

In order to make the measured dipole moments compatible with the calculated (Table I), a value μ_{NS} must be assumed for the N^-–S^+ bond such that $\vec{\mu}_{found} = \vec{\mu}_{calcd} + \mu_{NS}\vec{r}$ Squaring both sides of the equation and replacing by scalar quantities wherever appropriate, this is transformed into

$$\mu^2_{found} = \mu^2_{calcd} + \mu^2_{NS} + 2\mu_{NS}\vec{\mu}_{calcd} \cdot \vec{r} \qquad (1)$$

Solving this quadratic equation for μ_{NS} one gets

$$\mu_{NS} = -(\vec{\mu}_{calcd} \cdot \vec{r}) \pm [(\vec{\mu}_{calcd} \cdot \vec{r})^2 + \mu^2_{found} - \mu^2_{calcd})]^{1/2} \qquad (2)$$

and the dot-product of the vectors is readily computed for each X substituent from the data in Table II as

$$\vec{\mu}_{calcd} \cdot \vec{r} = \mu_x r_x + \mu_y r_y + \mu_z r_z$$

The values for μ_{NS} in Table I are calculated in this fashion. [The second root (2) of the quadratic equation (1) gives a large moment in the wrong direction (^+N–S^-) and was discarded.]

In the course of this work we also measured the dipole moments of p-$CH_3C_6H_4SO_2NS(CH_3)_2$, 7.46 D; p-$O_2NC_6H_4CONS(CH_3)_2$, 7.7 D; and o-$NCC_6H_4NS(CH_3)_2$, 6.29 D.

Discussion

Both the calculation of the S–N bond dipole and its interpretation are subject to some uncertainties. The assumption that the C(Ar)–X bond moment is the same as in para-substituted aniline is undoubtedly not strictly valid, since the negative charge on nitrogen in an N-aryliminosulfurane may well enhance the aromatic resonance over that of aniline. The fact that the calculated μ_{NS} increases from the p-fluoro to the p-nitro substituted compound by as much as 1.05 D (Table I, last column) may in part be an artifact resulting from the C–F, C–Cl, and C–Br dipoles being diminished by the iminosulfurane moiety whereas the moments of CN and NO_2 may well be enhanced over those in the corresponding para-substituted aniline. As a consequence, the C–F, C–Cl, and C–Br dipoles used in the calculation may be too large and those of C–CN and C–NO_2 too small. The effect of making an appropriate correction would be to diminish the μ_{NS} contribution in the latter two cases and enhance it in the former two, i.e., it would tend to produce better agreement among the five values. The magnitude of this problem may be estimated as ±0.5 D from the overall range (ca. 1 D) of μ_{NS}.

A second difficulty results from the assumption of constant geometry in all five iminosulfuranes investigated. If, indeed, as Table I suggests, the dipolar form contributes most in the p-nitro compound the N–S bond length might be expected to be greatest in that compound and somewhat less in the others in which the N–S bond has less polar character. The effect of this correction would be small, however, since the variation in bond length is unlikely to exceed 0.02 Å.

A third difficulty stems from the assumption (made in all calculations of this type) that group moments are transferable from one type of compound to another, i.e., that μ_{anil} is the same in aniline and in N-phenyl-S,S-dimethyliminosulfurane. This assumption is unavoidable; since the moment in question (0.95 D) is relatively small, the potential error is probably small also.

From the μ_{NS} bond moments one can calculate percent ionic character of the bond by making the customary[20] (though not strictly correct) assumption that a nonionic N–S bond has zero dipole moment. A bond 1.651 Å in length (Figure 1) and having separation of one electronic charge has a dipole moment of 4.80 × 1.651 = 7.93 D. By dividing this figure into the calculated N–S bond moment one obtains the percentage ionic character as follows: p-F, 45.2%; p-Cl, 47.3%; p-Br, 50.6%; p-CN, 55.5%; p-NO_2, 58.4%. This calculation, like that of μ_{NS} (vide supra), is subject to some uncertainty owing to the possible slight variation in the N–S bond length; fortunately, the effect of changing N–S on the μ_{NS} and its effect on the calculation of the percent ionic character tend to cancel one another. The limitations of the assumption that a N=S double bond has zero dipole moment may be gauged in two ways. Pauling[20] gives a value of 3.0 for the electronegativity of nitrogen, 2.5 for sulfur. The calculated percent ionic character[20] for this difference in electronegativity for a single bond would be 6% corresponding to a dipole moment of 0.5 D (N^-–S^+). A different N–S dipole may be estimated by taking the difference between C–N and C–S dipole moments; this difference ranges from 0.34 (1.6 − 1.26)[28] to 0.5 (0.95 − 0.45)[32] but makes the sulfur the *more negative* atom. The likely conclusion is that neutral N–S would probably have a very small dipole moment ($|\mu| \leq 0.5$ D) which would affect the calculation of the contribution of the N^-–S^+ resonance hybrid by no more than 6%.

In conclusion, taking into account the observed variations of μ_{NS} (Table I) and the other uncertainties discussed, the percent ionic character of the N–S bond in ArN^-–$S^+Me_2 \leftrightarrow ArN{=}SMe_2$ would seem to range from 40 to 60% depending on the substituent on the aromatic ring. The mean value, 50 ± 10%, agrees well with that found by x-ray photoelectron spectroscopy[14] (55%) and suggests that the bonding is about half covalent. The ionic contribution is substantially greater than that in the sulfoxide (^+S–O^-) bond, calculated to be 34.5% from the dipole moment of dimethyl sulfoxide by a procedure similar to the above.

The question as to whether the covalent contribution is due to $p\pi$–$d\pi$ bonding (a type of bonding not presently favored by molecular orbital calculations[33]) or to π–σ^* bonding[34] remains open.

Experimental Section

Crystal Data. $C_8H_{10}N_2O_2S$, mol wt 198.2. Monoclinic, $a = 4.845$ (4), $b = 9.886$ (7), $c = 21.018$ (10) Å, $\beta = 109.49$ (10)°, $U = 949.0$ Å^3, d_m (flotation) = 1.39 g cm^{-3}, $Z = 4$, $d_c = 1.387$ g cm^{-3}, g cm^{-3}, F (000) = 416. Mo Kα radiation, $\lambda = 0.7107$ Å; absorption coefficient for Mo Kα radiation, $\mu = 3.1$ cm^{-1}. Space group uniquely established as $P2_1/c$ ($C_{2h}{}^5$) from the systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

Crystallographic Measurements. Preliminary cell dimensions and space group data were obtained from precession photographs taken with Mo Kα radiation and Weissenberg photographs taken with Cu Kα ($\lambda = 1.542$ Å) radiation. A crystal of dimensions ca. 0.20 × 0.20 × 0.40 mm was oriented on a glass fiber such that the a^* axis was parallel to the ϕ axis of an Enraf-Nonius CAD 3 diffractometer (Zr-filtered Mo Kα radiation, take-off angle 3°). Improved cell parameters were obtained by least-squares treatment of the θ, χ, and ϕ values of 30 accurately centered reflections widely separated in reciprocal space. All unique intensity data up to $\theta = 25°$ were recorded using the θ–2θ scanning technique with scanwidths (0.90 + 0.45 tan θ) deg. Attenuators were inserted automatically to ensure that counting rates did not exceed 2500 counts per second; attenuation factors were derived experimentally. Stationary background measurements were made at each end of the scan range for a time equal to half the scan period. A standard reflection remeasured after each batch of 99 reflections showed no significant variation of intensity during the data collection. From a total of 1706 measurements, 823 reflections for which $I > 2.0\sigma(I)$, where $\sigma(I)$ = (scan count + total background count)$^{1/2}$, were used in the structure analysis and refinement. Absorption errors were shown to be insignificant by examination of the ϕ dependence of the strong 100 axial reflection measured at $\chi = 90°$. The data were corrected for the usual Lorentz and polarization effects.

Structure Analysis. The structure was solved by the heavy-atom method. Initial coordinates for the sulfur atom were derived from the three-dimensional Patterson map, and positions for the other nonhydrogen atoms were obtained from the sulfur-phased (R 0.502) F_o Fourier synthesis. Several cycles of full-matrix least-squares refinement at first with isotropic, and subsequently with anisotropic, thermal parameters reduced R from 0.22 to 0.091. Hydrogen atom positions were then located in a difference Fourier synthesis and their positional and isotropic thermal parameters were refined along with the parameters of the nonhydrogen atoms in all further least-squares calculations. The refinement converged at R 0.050 when no parameter shift exceeded 0.10 times its standard deviation. The positional and thermal parameters derived from the final least-squares cycle are included in the supplementary material.[31]

In the structure-factor calculations scattering factors for C, N, O, and S were taken from the Cromer and Waber[35] compilation, and for H the Stewart, Davidson, and Simpson[36] values were used. In the least-squares calculations $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$) was minimized with weights w assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| < 16.0$ and $\sqrt{w} = 16.0/|F_o|$ for $|F_o| > 16.0$; this scheme showed no systematic dependence of $\langle w\Delta^2 \rangle$ when analyzed in ranges of $|F_o|$ and $\sin\theta$ and consequently was considered satisfactory.

Fractional coordinates and anisotropic thermal parameters for nonhydrogen atoms are given in Table III in the Appendix,[31] corresponding data for hydrogen atoms in Table IV. Table V[31] gives orthogonal coordinates required for the dipole calculations.

Dipole Moment Determinations. The dilute solution method was used. For each compound, five solutions of different concentration (mole fraction less than 0.005) were made up. Spectrograde solvents were dried over 4 Å molecular sieves. The dielectric constants of benzene or dioxane solutions were measured at 25.0 °C using the Dipole Meter DM 01 manufactured by Wissenschaftliche Technische Werkstätten. The dipole moments were calculated according to the method of Higasi[27] by formula

$$\mu = \beta\left[\frac{M_1}{M_2}(\mathrm{d}\epsilon/\mathrm{d}w)\right]^{1/2}$$

where β is a constant, M_1 and M_2 are the molecular weights of the solvent and the solute, respectively, and $\mathrm{d}\epsilon/\mathrm{d}w$ denotes the initial slope of the plotted curve of dielectric constant vs. weight fraction w. For benzene solutions $\beta = 0.8481$ and for dioxane $\beta = 0.8429$ were used.[37] The slopes $\mathrm{d}\epsilon/\mathrm{d}w$ were determined by the least-squares method. The standard deviations of the slopes were used to calculate the standard deviations of the dipole moments. The dielectric data are tabulated in the Appendix,[31] Table VI.

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Registry No.—I, 27691-52-7; II, 52259-89-9; III, 20094-95-5; IV, 27691-48-1; V, 39159-87-0; VI, 52259-88-8; VII, 52259-85-5; VIII, 13150-75-9; *p*-aminobenzonitrile, 873-74-5.

Supplementary Material Available. Tables of atomic coordinates (Tables III–V), dielectric data used in the calculation of dipole moments (Table VI), and the program used in the computation of dipole moments (Table VII) (5 pages). Ordering information is given on any current masthead page.

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