Conformation of Substituted Arylureas. Crystal Structures of *N,N'*-Dimethyl-*N,N'*-di(*p*-nitrophenyl)urea and *N,N'*-Dimethyl-*N,N'*-di(2,4-dinitrophenyl)urea

U. Lepore, G. Castronuovo Lepore, and P. Ganis

Istituto Chimico, Universita di Napoli, 80134 Napoli, Italy

G. Germain

Laboratoire de Chimie Phisique et Cristallographie, Batiment Lavoisier, Université de Louvain, Louvain-la-Neuve, Belgium

M. Goodman*

Department of Chemistry, University of California, San Diego, La Jolla, California 92093

Received November 17, 1975

In this paper we report a comparison between the conformation in solution and in the solid state of *N,N'*-dimethyl-*N,N'*-di(*p*-nitrophenyl)urea and *N,N'*-dimethyl-N,N'-di(2,4-dinitrophenyl)urea. The synthesis and the NMR spectrum for the latter compound are reported. Also, the crystalline structure of the two compounds is presented. The former compound crystallizes in the space group *C*2/*c* with unit cell constants a = 8.17 (1) Å, b = 14.94 (1) Å, c = 12.43 (1) Å, β = 94.6 (2)°, Z = 4. The latter compound crystallizes in the space group *Pbcn* with unit cell constants a = 6.89 (1) Å, b = 10.32 (1) Å, c = 24.00 (2) Å, Z = 4. The structures were solved by direct methods and refined by block-diagonalized-matrix, least-squares calculations to reliability indices of 0.097 and 0.093, respectively. In the former compound the phenyl groups are anti to the carbonyl oxygen, while in the latter the phenyl rings are syn to the carbonyl oxygen. Both the compounds show a nonplanar distortion of the amide group. The structures are compared to similar compounds previously studied.

A spectroscopic study of substituted arylureas in solution has been recently undertaken in order to investigate the nature of the forces leading to the "stacking" of aromatic rings in these compounds.[1] NMR and uv spectra supported the hypothesis that phenyl–phenyl interactions could be responsible for this behavior, depending on the nature of the substituents bonded to the phenyl rings. The previously reported structure of *N,N'*-diethyl-*N,N'*-diphenylurea (I)[2] showed phenyl rings facing each other and partially overlapping so that very short contact distances between ring atoms were observed. On the basis of NMR and uv spectra, we expected that *N,N'*-dimethyl-*N,N'*-di(*p*-nitrophenyl)urea (II) would have a conformation similar to that of compound I, but with the phenyl rings closer to each other. This fact may be predicted by inferring electron withdrawal by the nitro groups. For the same reason we also would expect the phenyl rings of a compound such as *N,N'*-dimethyl-*N,N'*-di(2,4-dinitrophenyl)urea (III) to be even closer. Therefore we synthesized and characterized compound III, and undertook the analysis of the crystalline structure of both compounds II and III in order to study further the interactions between the two aromatic rings in these molecules. We also compared the conformation of the amide groups with that found in similar compounds.[3]

Experimental Section

***N,N'*-Dimethyl-*N,N'*-di(*p*-nitrophenyl)urea (II).** This compound was prepared according to the procedure described in ref 1. The crystals have a prismatic shape. A similar crystal was chosen with dimensions 0.15 × 0.20 × 0.20 mm. Weissenberg photographs showed that the crystal is monoclinic with possible space groups *Cc* or *C*2/*c*. (The following structural investigation confirmed the space group to be *C*2/*c*.) The crystal was mounted on a Picker automated diffractometer with the b axis parallel to the spindle axis. The unit cell constants were determined from a least-squares fit of the angular positions of 12 independent reflections. They are reported in Table IA. No attenuators were used. A take-off angle of 3°, a 2θ–θ scan mode, and a scan range of 1.67° were used for data collection. The peak was scanned for 100 s and backgrounds on either side of the peak were measured for 10 s. Data were taken to a 2θ value of 45° with Zr-filtered Mo K$_\alpha$ radiation. We collected 1415 independent reflections, 112 of which were considered unobserved since the number of counts for them was less than 200. No absorption corrections were applied.

Table I. Unit Cell Constants

A. *N,N'*-Dimethyl-*N,N'*-di(*p*-nitrophenyl)urea (II)

a = 8.17 (1) Å	V = 1512.2 Å^3
b = 14.94 (1) Å	Z = 4
c = 12.43 (1) Å	d_x = 1.46 g cm^{-3}
β = 94.6 (2)°	d_o = 1.44 g cm^{-3}
Space group *C*2/*c*	

B. *N,N'*-Dimethyl-*N,N'*-di(2,4-dinitrophenyl)urea (III)

a = 6.89 (1) Å	V = 1706.0 Å^3
b = 10.32 (1) Å	Z = 4
c = 24.00 (2) Å	d_x = 1.62 g cm^{-3}
Space group *Pbcn*	d_o = 1.58 g cm^{-3}

***N,N'*-Dimethyl-*N,N'*-di(2,4-dinitrophenyl)urea (III).** It has been reported[4] that the nitration of *N,N'*-diphenylurea by 68.28% HNO_3 in concentrated sulfuric acid at 0 °C gives *N,N'*-di(*p*-nitrophenyl)urea, and no tetranitro derivative was detected. In our case, in the same experimental conditions, starting with *N,N'*-dimethyl-*N,N'*-diphenylurea, only the tetranitro derivative was obtained, probably because of the acetamido-like substitution that makes the rings more electron rich (more active toward electrophilic aromatic substitution). One gram (4 mmol) of *N,N'*-dimethyl-*N,N'*-diphenylurea was dissolved in concentrated sulfuric acid. Nitric acid (69%) was added at 0 °C and the solution was stirred for approximately 1 h. After addition of water, a yellow precipitate was obtained (90% yield). The melting point of the crude derivative was 189 °C. After crystallization from acetone, the melting point was raised to 195 °C.

Anal. Calcd for $C_{15}H_{12}N_6O_9$: C, 42.85; H, 2.85; N, 20.00. Found: C, 42.88; H, 2.84; N, 20.10.

Nuclear magnetic resonance spectra were measured on a Varian 220-MHz spectrometer using tetramethylsilane as the internal standard.

The NMR spectrum of the tetranitrourea, reported in Figure 1, was studied in acetone and acetonitrile (Table II) over a wide range of concentrations (5–0.1%) and showed no significant variation in chemical shifts. The temperature dependence of the spectrum was also studied: no changes in the coupling constants or in the chemical shifts were observed over the temperature range −30 to 35 °C. Moreover, at the lower temperatures the spectra showed no splitting into bands or broadening of the signals. These results seem to indicate that in solution there is a strong preponderance of one isomer.

Crystals of this compound are needle shaped. Weissenberg pho-

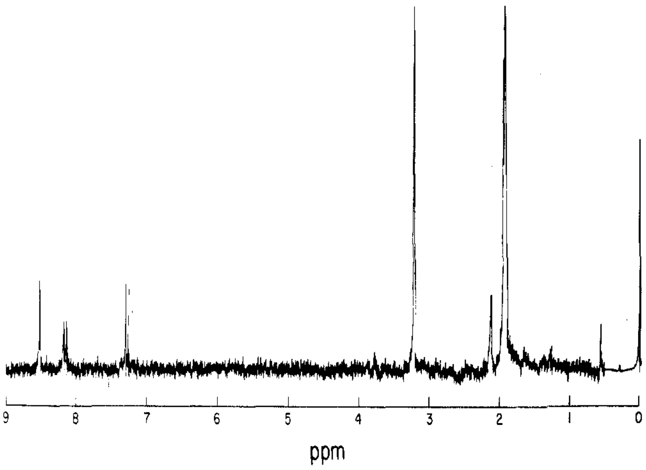


Figure 1. Nuclear magnetic resonance spectra at 220 MHz in parts per million for *N,N′*-dimethyl-*N,N′*-di(2,4-dinitrophenyl)urea in CD_3CN at 25 °C.

Table II. Chemical Shifts[a] of the Methyl Groups and Aromatic Protons of *N,N′*-Dimethyl-*N,N′*-di(2,4-dinitrophenyl)urea in Deuterated Acetone and Acetonitrile

CD_3COCD_3	3.34	7.54	8.32	8.63
CD_3CN	3.23	7.27	8.16	8.50

[a] In parts per million.

tographs indicate the space group *Pbcn*. A single crystal was mounted on a Picker automated diffractometer and the unit cell constants were calculated from the setting of 12 reflections by least-squares procedures. They are reported in Table IB. No attenuators were used. A take-off angle of 3°, a 2θ–θ scan mode, and a scan range of 1.67° were used for data collection. The scan range was chosen because some peaks were nearly 1.5° wide. The peak was scanned for 100 s and backgrounds on either side of the peak were measured for 10 s. Intensities for 1808 independent reflections were measured using Zr-filtered Mo K_α radiation to a 2θ value of 45°; 479 of them were considered unobserved since the number of counts for them was less than 200.

Determination of the Structures and Refinement. The structures were solved by weighted multisolution tangent refinement.[5] The largest 130 *E*'s were used for II and 160 for III. The starting set of phases selected by iterative procedure (CONVERGE) yielded 25 possible solutions both for II and III. One set of phases for II and one set of phases for III seemed to be correct; the corresponding *E* maps revealed the whole structure. The atomic positions and isotropic thermal parameters were refined by a few cycles of block-matrix, least-squares calculations[7] to an $R = 0.180$ and an $R = 0.166$ for II and III, respectively. Further cycles including anisotropic thermal parameters and the geometrically located hydrogen atoms reduced *R* to the final value of 0.097 and 0.093 for II and III, respectively. In both cases the hydrogen coordinates were not refined and their isotropic thermal parameter was assumed constant and equal to 3 Å^2; the function minimized was $(wF_c - KF_o)^2$ and the form of Cruickshank's weighting function was $w = 0.11111 + 0.01243\,F_{o_{min}} + 1.9888 \times 10^{-4}\,F_{o_{max}}$. The atomic scattering factors were taken from Moore.[6] The final positional and thermal parameters are listed in Table III (microfilm supplement).[8]

Description of the Structures. The relevant internal coordinates of the molecules of II and III are reported in Figures 2 and 3 and in Tables IVA and B. Both the molecules are characterized by a C_2 symmetry.

A comparison between the conformation of I and II shows that the phenyl groups, which in both cases are anti to the oxygen and in a stacked position near one another, are closer for compound II than in the case of compound I. The distance between the centers of the phenyl groups is 3.90 Å for I and 3.80 Å for II; the dihedral angle between the phenyl planes is about 3° wider in I than in II, while the lateral displacement of such planes from one another is about the same. In Table V the phenyl-phenyl contact distances for II, shorter than 4 Å, are compared with the corresponding distances for I.

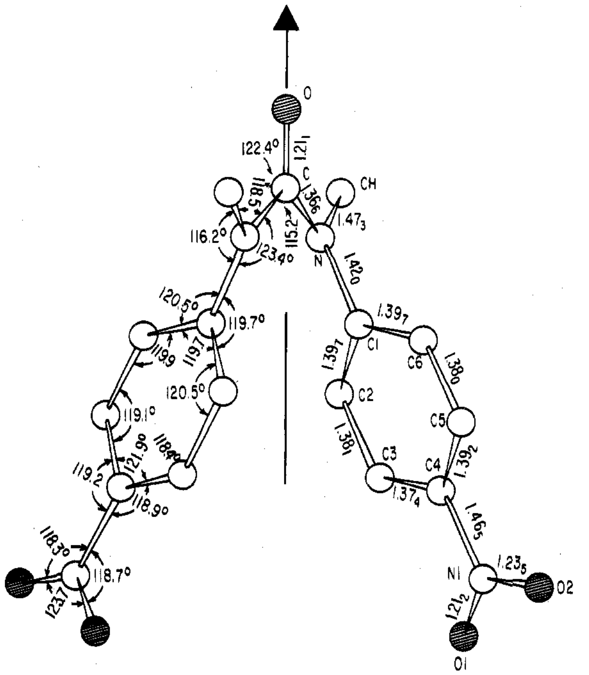
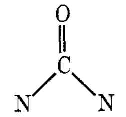


Figure 2. Schematic representation of the molecule of *N,N′*-dimethyl-*N,N′*-di(*p*-nitrophenyl)urea (II).

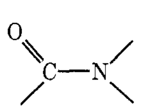
The bond angle



is smaller in II (115.2°) than in I (117.8°). Apart from this, the overall conformations of I and II are very similar. Owing to the electron withdrawal in the dinitro derivative, the phenyl–phenyl repulsive interactions are weakened so that the rings face each other more closely. Since there is evidence that such a rather rigid conformation is maintained in solution almost unchanged,[1] the reported results can be considered to be in agreement with the NMR analysis. In fact, the ring current seems to be lowered and a smaller upfield shift of the H ortho to the NO_2 group is observed.

In contrast, the molecular conformation of III shows that the phenyl rings are syn to the oxygen. One can easily check by using models that in a conformation anti to the oxygen the two ortho positions on the two phenyl rings would be hindered because of severe steric interactions which do not occur in the case of compound II. Thus, in spite of the strong $CH_3\cdots CH_3$ interaction 2.11 Å apart, the conformation assumed seems to be more relaxed, and the only stable one which also exists in solution. This is supported by the temperature dependence of the NMR spectra.

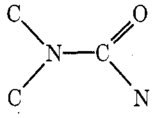
The torsion angles about the amide bond



for I, II and III are

	I	II	III
α = O–C–N–C1	208°	211°	21°
β = O–C–N–CH_3 (or C_2H_5)	5°	15°	224°
$\lvert\alpha - \beta\rvert$	203°	196°	203°

In all cases, the nonplanar distortion of the system



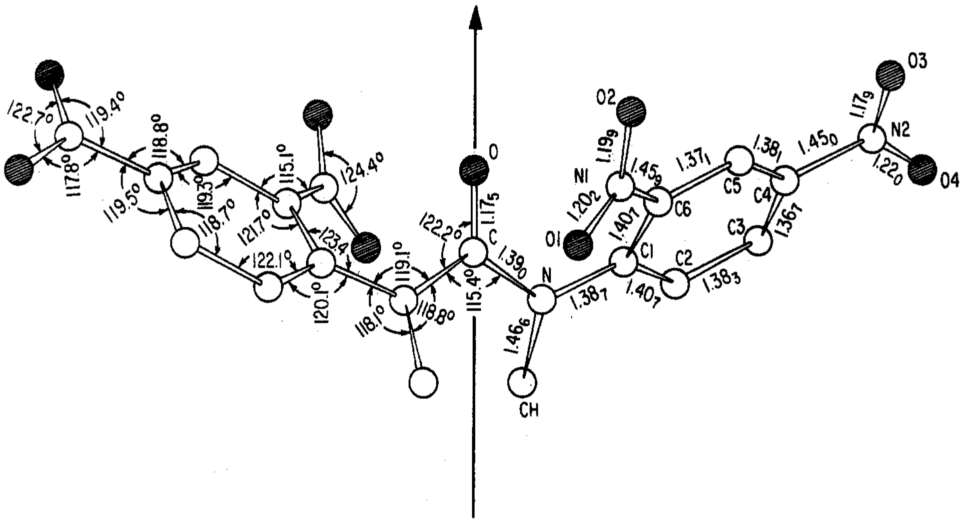


Figure 3. Schematic representation of the molecule of *N,N′*-dimethyl-*N,N′*-di(2,4-dinitrophenyl)urea (III).

Table IV

Distances, Å		Angles, deg		Torsion angles, deg	
A. Molecular Conformational Parameters of *N,N′*-Dimethyl-*N,N′*-di(*p*-nitrophenyl)urea (II)[a]					
O–C	1.211 (6)	N–C–N′	115.2 (1)	O–C–N–C(CH$_3$)	14.7
C–N	1.366 (3)	O–C–N	122.4 (1)	O–C–N–C1	210.8
N–C(CH$_3$)	1.473 (4)	C–N–C(CH$_3$)	118.5 (1)	C–N–C1–C2	224.3
N–C1	1.420 (4)	C–N–C1	123.4 (1)	C–N–C1–C6	47.7
C1–C2	1.397 (4)	C(CH$_3$)–N–C1	116.2 (1)	C(CH$_3$)–N–C1–C2	60.0
C2–C3	1.381 (5)	N–C1–C2	119.7 (1)	C(CH$_3$)–N–C1–C6	243.4
C3–C4	1.374 (5)	N–C1–C6	120.5 (1)	C3–C4–N1–O1	1.6
C4–C5	1.392 (5)	C1–C2–C3	120.5 (2)	C3–C4–N1–O2	181.1
C5–C6	1.380 (5)	C2–C3–C4	118.4 (2)	C5–C4–N1–O1	181.0
C6–C1	1.397 (4)	C3–C4–C5	121.9 (2)	C5–C4–N1–O2	0.5
C4–N1	1.465 (4)	C4–C5–C6	119.1 (2)	C(CH$_3$)–N–C–N′	194.8
N1–O1	1.212 (4)	C5–C6–C1	119.9 (1)	C1–N–C–N′	30.8
N1–O2	1.235 (4)	C6–C1–C2	119.7 (1)		
		C3–C4–N1	118.9 (1)		
		C5–C4–N1	119.2 (1)		
		C4–N1–O1	118.7 (2)		
		C4–N1–O2	118.3 (2)		
		O1–N1–O2	123.0 (2)		
B. Molecular Conformational Parameters of *N,N′*-Dimethyl-*N,N′*-di(2,4-dinitrophenyl)urea (III)[a]					
O–C	1.175 (6)	O–C–N	122.2 (1)	O–C–N–C(CH$_3$)	223.7
C–N	1.390 (4)	C–N–C(CH$_3$)	118.8 (2)	O–C–N–C1	21.1
N–C(CH$_3$)	1.466 (6)	C–N–C1	119.1 (2)	C–N–C1–C2	218.4
N–C1	1.387 (5)	C(CH$_3$)–N–C1	118.1 (2)	C–N–C1–C6	39.4
C1–C2	1.407 (6)	N–C1–C2	120.1 (2)	C(CH$_3$)–N–C1–C2	15.9
C2–C3	1.383 (7)	C1–C2–C3	122.1 (2)	C(CH$_3$)–N–C1–C6	196.9
C3–C4	1.367 (7)	C2–C3–C4	118.7 (2)	N–C1–C6–N1	8.9
C4–C5	1.381 (6)	C3–C4–C5	121.6 (2)	C4–C5–C6–N1	170.5
C5–C6	1.371 (5)	C4–C5–C6	119.3 (2)	C1–C6–N1–O1	29.3
C6–C1	1.407 (5)	C5–C6–C1	121.7 (2)	C1–C6–N1–O2	208.9
C6–N1	1.459 (5)	C6–C1–C2	116.4 (2)	C5–C6–N1–O1	214.7
N1–O1	1.202 (5)	C6–C1–N	123.4 (2)	C5–C6–N1–O2	34.2
N1–O2	1.199 (6)	C1–C6–N1	122.9 (2)	C6–C5–C4–N2	183.1
C4–N2	1.450 (5)	C5–C6–N1	115.1 (2)	C2–C3–C4–N2	179.8
N2–O3	1.179 (6)	C6–N1–O1	119.2 (2)	C5–C4–N2–O3	−17.0
N2–O4	1.220 (5)	C6–N1–O2	116.4 (2)	C5–C4–N2–O4	164.0
		O1–N1–O2	124.4 (2)	C3–C4–N2–O3	164.8
		C4–N2–O3	119.4 (2)	C3–C4–N2–O4	−14.2
		C4–N2–O4	117.8 (2)	C(CH$_3$)–N–C–N′	43.8
		O3–N2–O4	122.7 (2)	C1–N–C–N′	201.2
		C3–C4–N2	119.5 (2)		
		C5–C4–N2	118.8 (2)		
		N–C–N′	115.4 (2)		

[a] Standard deviations are indicated in parentheses.

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.

Acknowledgment. We gratefully acknowledge financial support of this work by a grant from the National Science Foundation (GP 35810).

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.

References and Notes

(1) G. Lepore, S. Migdal, D. E. Blagdon, and M. Goodman, *J. Org. Chem.*, **38**, 2590 (1973).

(2) P. Ganis, G. Avitabile, E. Benedetti, C. Pedone, and M. Goodman, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 426 (1970).

(3) P. Ganis, G. Avitabile, S. Migdal, and M. Goodman, *J. Am. Chem. Soc.*, **93**, 3328 (1971), and papers cited therein.

(4) I. M. Kogan and D. F. Kutepor, *Zh. Obshch. Khim.*, **21**, 1297 (1951).

(5) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

(6) F. H. Moore, *Acta Crystallogr.*, **16**, 1169 (1963).

(7) The programs written by A. Immirzi, *Ric. Sci.*, **37**, 743, 846, 850 (1967), were used for these calculations.

(8) The lists of the observed and calculated structure factors may be obtained from one of the authors.

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

Ernest L. Eliel,*[1a] Jorma Koskimies,[1a] Andrew T. McPhail,[1b] and Daniel Swern[1c]

W. R. Kenan, Jr., Laboratories, University of North Carolina, Chapel Hill, North Carolina 27514, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, and Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received November 17, 1975

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, $p\text{-}CH_3C_6H_4SO_2NSMe_2$, 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.