373K, and 1.63 cal K^{-1} mol^{-1} at 393K. The broken curve goes through the smoothed values from Table IV of Criss and Cobble (*3*), represented by the circles. Any smooth curve through these points must have a peculiar inflection near 323K.

The agreement between the values of Criss and Cobble and those computed from experimental heat capacities and our equation is remarkable. Even more remarkable is that when calorimetric quantities at 298K are omitted and all of the parameters of our equation are determined from solvent activities, the maximum deviation from Criss and Cobble is only 3.0 cal K^{-1} mol^{-1}. This requires that the fourth derivative of G^E/RT with respect to temperature be approximately correct. This is possible only for an equation derived from accurate solvent activities over a wide temperature range.

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NEW COMPOUND SECTION

Synthesis and Spectral Data for Some Derivatives of *N*-Aryloxamic Acid Hydrazides

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By condensation of diethyl oxalate with aromatic amines, 21 ethyl *N*-aryloxamates were prepared. Subsequent reaction with hydrazine afforded the corresponding *N*-aryloxamic acid hydrazides; these were converted into 80 hydrazones, 10 *N*-phosphoryl, 26 *N*-sulfonyl, nine *N,N*-dimethylcarbamoyl, and six *N*-ethoxycarbonyl derivatives. The ir and nmr spectral data of the various compounds and their biological activities are presented.

The *N*-aryloxamic acid hydrazides (I) (Table II) were obtained by hydrazinolysis of the appropriate ethyl *N*-aryloxamate (II) (Table I) (*24*). The latter were prepared by condensation of the arylamine with diethyl oxalate following the method of Pierce et al. (*22*):

$$(CO_2C_2H_5)_2 \xrightarrow{RNH_2} \underset{(II)}{R{\cdot}NH{\cdot}COCO_2C_2H_5} + \underset{(IV)}{RNHCOCONHR}$$

$$\underset{(II)}{R{\cdot}NH{\cdot}COCO_2C_2H_5} \xrightarrow{N_2H_4H_2O} \underset{(I)}{RNH_a{\cdot}COCO{\cdot}NH_bNH_2} \xrightarrow{R'R''CO} \underset{(III)}{RNHCOCONHN{=}CR'R''}$$

The hydrazides (I) were converted into hydrazones (III) (Table III) by treatment with the appropriate carbonyl compound: the reaction was catalyzed by a trace of io-

dine (27). o-Nitrobenzaldehyde, benzylideneacetone, and cinnamaldehyde oxanilic acid hydrazones were photochromic (white or cream → yellow or orange on exposure to uv light).

Some of the hydrazides (I) were converted into the corresponding *N*-phosphoryl (Table IV), *N*-sulfonyl (Table V), *N,N*-dimethylcarbamoyl (Table VI), and *N*-ethoxycarbonyl derivatives (Table VI). These derivatives were, respectively, of interest as potential insecticides (9), fungicides (8), and herbicides (11).

The ir spectra of ethyl *N*-aryloxamates (Table I) showed a strong, generally sharp, N—H stretching absorption in the region 3370–3220 cm^{-1} (3) and two strong carbonyl bands at 1740–1715 ($CO_2C_2H_5$) and 1715–1690 (CONH) cm^{-1}. The slightly higher value of the frequency of the latter absorption (3) is probably due to the presence of the aromatic ring on the amide nitrogen atom.

The *N*-aryloxamic acid hydrazides (Table II) showed two strong N—H stretching bands in the regions 3360–3280 and 3330–3180 cm^{-1}, together with a generally single amide carbonyl absorption appearing at a lower range of 1690–1665 cm^{-1} as compared with the oxamates, probably associated with the more effective electron-releasing power of the hydrazino group.

The corresponding hydrazones (Table III) exhibited two similar N—H bands in the same regions, indicating that these absorptions are probably associated with the amide and hydrazino NH groups rather than the NH_2 group; the amine carbonyl band is similar to that of the hydrazides so that both the hydrazides and the hydrazones generally only show one carbonyl ir band. The *N*-phosphoryl derivatives (Table IV) showed additional bands at 1240–1220 (P=O) or 740, 710 (P=S) (4); otherwise, the NH and CO bands are similar to those of the hydrazides.

The ir spectra of the *N*-sulfonyl derivatives (Table V) contained two additional bands at 1365–1330 and 1175–1160 cm^{-1}, arising from the S—O stretching vibrations in the SO_2 group (5). These compounds also usually showed two carbonyl bands in the regions 1730–1710 and 1690–1670 cm^{-1}, indicating that the introduction of the arylsulfonyl group has sufficiently altered the environment of the two carbonyl groups so that they give rise to two distinct absorption bands.

The *N,N'*-dimethylcarbamoyl derivatives (Table VI) also showed two carbonyl bands, though at lower frequencies (1690–1675 and 1670–1650 cm^{-1}). The ethoxycarbonyl derivatives (Table VI) showed only one N—H stretching absorption in the region 3290–3280 cm^{-1}, reflecting the much more similar environment of the NH groups in these compounds, which also showed two carbonyl bands at 1730–1725 ($CO_2C_2H_5$) and 1680–1655 cm^{-1} (CONH).

No clear correlation could be observed between the nature of the substituents attached to the aromatic nucleus and the carbonyl stretching frequencies, owing to the complex nature of the spectra, as has been observed (6) with substituted urea derivatives.

The nmr spectra of the ethyl oxamates (II) (Table I) showed normal signals for the ethyl group, but the NH proton signals appeared at very low field (0.6–0.9 τ). This results from the deshielding effect of the aromatic nucleus which is enhanced by the powerful electron-withdrawing influence of the adjacent carbonyl function, and the introduction of electron-withdrawing substituents into the aromatic nucleus moved the NH proton signal slightly further downfield (Table I). In the *N*-aryloxamic acid hydrazides (Table II) (I), the proton (Ha) of the amino group directly attached to the aromatic nucleus is more strongly deshielded than the proton (Hb), and these two protons generally give separate signals in the regions of

Table I. Physical Properties and Spectral Data for Ethyl *N*-Aryloxamates[a]

R—NH—CO·$CO_2C_2H_5$

(II)

Molecular formula	R	Mp, °C	Yield, %	Ir spectra		Nmr spectra[b]	
				νN—H, cm^{-1}	νC=O, cm^{-1}	NH τ	ArH τ
$C_{10}H_{11}NO_3$	C_6H_5	66–68 [lit. (22) 66–67]	64	3370 br	1730, 1710	0.8[c]	2.2–2.8 (5)
$C_{11}H_{13}NO_3$	2-MeC_6H_4	33–40 [lit. (21) 40]	34	3365	1740, 1715	0.8[d]	2.1–2.8 (4)
$C_{11}H_{13}NO_3$	3-MeC_6H_4	60–61 [lit. (18) 60–61]	37	3360	1740, 1715	0.8[d]	2.1–3.9 (4)
$C_{11}H_{13}NO_3$	4-MeC_6H_4	67–69 [lit. (13) 66–67]	35	3360	1740, 1715	0.9[d,e]	2.3–3.1 (4)
$C_{10}H_{10}N_2O_5$	2-$NO_2C_6H_4$[f]	112 [lit. (12) 112–113]	90	3220 br	1730, 1700	0.6	1.2–2.0 (4)
$C_{10}H_{10}N_2O_5$	3-$NO_2C_6H_4$	151–152 [lit. (1) 147–149.5]	64	3280	1730, 1700	0.7	1.4–2.6 (4)
$C_{10}H_{10}N_2O_5$	4-$NO_2C_6H_4$	168–169 [lit. (23) 170–171]	41	3340	1730, 1710	0.6[e]	1.6–2.2 (4)
$C_{11}H_{13}NO_4$	2-$MeOC_6H_4$	83–85 [lit. (16) 83.5]	52	3380	1725, 1710		
$C_{11}H_{13}NO_4$	3-$MeOC_6H_4$	96–98 [lit. (17) 97]	67	3370	1725, 1710		
$C_{11}H_{13}NO_4$	4-$MeOC_6H_4$	105–108 [lit. (26) 107–109]	88	3280	1730, 1715		
$C_{10}H_{10}ClNO_3$	2-ClC_6H_4	50 [lit. (14) 42–45]	16	3310	1715, 1710	0.7	2.2–2.8 (4)
$C_{10}H_{10}ClNO_3$	3-ClC_6H_4	110 [lit. (23) 113–114]	87	3330	1715, 1700	0.8	2.2–2.9 (4)
$C_{10}H_{10}ClNO_3$	4-ClC_6H_4	150–152 [lit. (7) 155]	75	3270	1725, 1690	0.7[e]	2.2–2.8 (4)
$C_{16}H_{13}N_3O_3$	4-C_6H_5-N_2-C_6H_4	160–162[g]	55	3350	1730, 1705		
$C_{10}H_9Cl_2NO_3$	2,4-$Cl_2C_6H_3$	118–119 [lit. (7) 119]	50	3340	1725, 1700	0.6	1.6–2.1 (3)
$C_{10}H_9Cl_2NO_3$	3,4-$Cl_2C_6H_3$	178–179 [lit. (2) 174]	60	3340	1730, 1700	0.7	1.7–2.2 (3)
$C_9H_{10}N_2O_3$	2-Pyridyl	72–73 [lit. (19) 71–73]	43	3220 br	1740, 1710	0.6	2.1–2.8 (4)
$C_9H_{10}N_2O_3$	3-Pyridyl	212–214	48	3330	1730, 1715		
$C_9H_{10}N_2O_3$	4-Pyridyl	226–228	10	3200 br	1725, 1710		
$C_{13}H_{12}N_2O_3$	3-Quinolyl	163–165	51	3340	1725, 1700		
$C_{16}H_{13}NO_3$	2-Biphenyl	120–122 [lit. (25) 112–113]	62	3370	1740, 1705		

[a] Elemental analyses (C,H,N) in agreement with theoretical values were obtained and submitted for review. [b] All compounds showed ethyl groups as a quartet CH_2 (5.5–5.6 τ) and a triplet CH_3 (8.6–8.7 τ). [c] *N,N'*-diphenyloxamide by-product had signals at −0.8 τ (2 NH) and 2.0–2.9 τ (10 ArH). [d] Methyl groups attached to aromatic nucleus signal at 7.7 τ. [e] ArH signals as two characteristic doublets. [f] Obtained by nitration of ethyl oxanilate (12). [g] Fawn plates.

−1.4 to −0.5 and −0.8 to −0.2 τ, respectively. The signals for Ha generally moved slightly further downfield when electron-withdrawing substituents were present in the aromatic nucleus (Table II). The protons of the primary amine group (NH_2) are much less deshielded and accordingly signaled at appreciably higher field (5.0–5.4 τ).

The nmr spectra of the acetone oxamic acid hydrazones (Table III) showed an additional sharp doublet (7.9, 8.1) owing to the protons of the $(C\underline{H}_3)_2C=$ group.

Table II. Physical Properties and Spectral Data for *N*-Aryloxamic Acid Hydrazides[a]

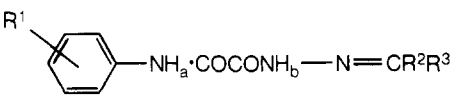
R—$NH_aCO\cdot CO\cdot NH_b$—NH_2

(I)

Molecular formula	R	Mp, °C	Yield, %	Ir spectra		Nmr spectra, τ			
				νN—H, cm^{-1}	νC=O, cm^{-1}	$N\underline{H}_a$	$N\underline{H}_b$	$N\underline{H}_2$	Ar$\underline{H}$
$C_8H_9N_3O_2$	C_6H_5	214–215 [lit. (*24*) 217]	68A	3330, 3310	1670	−0.6	−0.3	5.4	2.0–2.8 (5)
$C_9H_{11}N_3O_2$	2-MeC_6H_4	154	73A	3325, 3300	1720, 1675	−0.7 (2)[b]		5.5	2.2–2.9 (4)
$C_9H_{11}N_3O_2$	3-MeC_6H_4	152–153	90B	3320, 3310	1670	−0.5 (2)[b]		5.4	2.3–3.1 (4)
$C_9H_{11}N_3O_2$	4-MeC_6H_4	218–220 [lit. (*20*) 212–213]	89A	3320, 3280	1670	−0.6[b]	−0.2	5.3	2.1–2.9 (4)[c]
$C_8H_8N_4O_4$	2-$NO_2C_6H_4$	258–260[d]	28C	3300, 3260	1665	−1.2	−0.7	5.0	1.2–2.0 (4)
$C_8H_8N_4O_4$	3-$NO_2C_6H_4$	224–225[d]	79C	3325, 3280	1670	−1.0	10.5	5.3	1.6–2.4 (4)
$C_8H_8N_4O_4$	4-$NO_2C_6H_4$	243–244[d] [lit. (*24*) 273]	43C	3280, 3180	1670 br	−1.1	−0.6	5.2	1.3–1.7 (4)[c]
$C_8H_8ClN_3O_2$	2-ClC_6H_4	154–156 [lit. (*20*) 150–152]	70A	3300, 3250	1695	−1.1	−0.6	5.3	1.6–2.2 (4)
$C_8H_8ClN_3O_2$	3-ClC_6H_4	198 [lit. (*20*) 199–201]	85B	3340, 3290	1660	−0.8 (2)		5.3	1.8–2.3 (4)
$C_8H_8ClN_3O_2$	4-ClC_6H_4	273–275 [lit. (*20*) 265–268]	75D	3350, 3330	1700, 1670	−1.0 (2)		5.3	2.0–2.7 (4)[c]
$C_9H_{11}N_3O_3$	2-$MeOC_6H_4$	167–170 [lit. (*20*) 162–163]	62B	3360, 3310	1700, 1670 br				
$C_9H_{11}N_3O_3$	3-$MeOC_6H_4$	154–155	86A	3315, 3280	1670				
$C_9H_{11}N_3O_3$	4-$MeOC_6H_4$	236–238 [lit. (*20*) 228–230]	88A	3325, 3290	1670				
$C_{14}H_{13}N_5O_2$	4-$C_6H_5N_2C_6H_4$	270–272[e]	70A/E	3340, 3300	1670				
$C_8H_7Cl_2N_3O_2$	2,4-$Cl_2C_6H_3$	230–231 [lit. (*20*) 221–223]	70A	3300, 3240	1690				
$C_8H_7Cl_2N_3O_2$	3,4-$Cl_2C_6H_3$	253–255	70A	3320, 3280	1700, 1660				
$C_7H_8N_4O_2$	2-Pyridyl	190–193[f] [lit. (*20*) > 300]	65A	3340, 3280	1685	−1.4	−0.8	5.1	2.3–2.9 (4)
$C_7H_8N_4O_2$	4-Pyridyl	148–150	45B	3330, 3280	1680				
$C_{11}H_{10}N_4O_2$	3-Quinolyl	218–220	77B	3320, 3260	1690, 1665				
$C_{14}H_{13}N_3O_2$	2-Diphenyl	162–164	61A	3320, 3280	1665				

[a] Elemental analyses (C,H,N) in agreement with theoretical values were obtained and submitted for review. [b] Ar-$C\underline{H}_3$ signals at 7.7–7.8 τ. [c] Ar$\underline{H}$ signals as two characteristic doublets. [d] Cream prisms. [e] Orange plates. [f] Melts and resolidifies to a solid mp > 300°. Solvents used for crystallization: A, EtOH; B, MeOH; C, dioxan; D, tetrahydrofuran; E, dimethylformamide.

Table III. *N*-Aryloxamic Acid Hydrazones[a]



Molecular formula	R^1	R^2	R^3	Mp, °C	Yield, %	Ir spectra	
						νN—H, cm^{-1}	νC=O, cm^{-1}
$C_{11}H_{13}N_3O_2$	H	Me	Me	200–201 [lit. (*24*) 210][b]	68	3300 br	1670
$C_{15}H_{12}N_4O_4$	H	H	2-$NO_2C_6H_4$	250	61		
$C_{14}H_{17}N_3O_2$	H	—$(CH_2)_5$—		189–191	72		
$C_{16}H_{13}N_3O_2$	H	Me	C_6H_5	233 [lit. (*24*) 237]	53		
$C_{17}H_{13}N_3O_2$	H	H	C_6H_5CH=CH	228	52		
$C_{18}H_{17}N_3O_2$	H	Me	C_6H_5CH=CH	233–224	69		
$C_{15}H_{12}N_4O_4$	H	H	4-$NO_2C_6H_4$	225	61		
$C_{15}H_{13}N_3O_3$	H	H	2-OHC_6H_4	158–159	47		
$C_{15}H_{11}Cl_2N_3O_2$	H	H	3,4-$Cl_2C_6H_3$	166–168	55		
$C_{15}H_{13}N_3O_3$	H	H	4-OHC_6H_4	180–181	70		
$C_{12}H_{15}N_3O_2$	2-Me	Me	Me	141[c]	29	3280 br	1670
$C_{16}H_{14}N_4O_4$	2-Me	H	2-$NO_2C_6H_4$	260–262	82		
$C_{15}H_{19}N_3O_2$	2-Me	—$(CH_2)_5$—		161–162	42		
$C_{12}H_{15}N_3O_2$	3-Me	Me	Me	174–176	66		
$C_{15}H_{19}N_3O_2$	3-Me	—$(CH_2)_5$—		173–174	85		
$C_{16}H_{14}N_4O_4$	3-Me	H	2-$NO_2C_6H_4$	206–207	90		
$C_{16}H_{14}N_4O_4$	3-NO_2	Me	C_6H_5	221–224	37		
$C_{11}H_{12}ClN_3O_2$	2-Cl	Me	Me	131–132	41	3320, 3290	1670
$C_{15}H_{11}ClN_4O_4$	2-Cl	H	2-$NO_2C_6H_4$	229–231	52		

Table III. (Continued)

Molecular formula	R^1	R^2	R^3	Mp, °C	Yield, %	Ir spectra: νN—H, cm^{-1}	Ir spectra: νC=O, cm^{-1}
$C_{14}H_{16}ClN_3O_4$	2-Cl	—$(CH_2)_5$—		121–123	35		
$C_{11}H_{12}ClN_3O_2$	3-Cl	Me	Me	218–220	75	3300, 3280	1665
$C_{15}H_{11}ClN_4O_4$	3-Cl	H	2-$NO_2C_6H_4$	227–228	88		
$C_{14}H_{16}ClN_3O_2$	3-Cl	—$(CH_2)_5$—		210	55		
$C_{16}H_{14}ClN_3O_2$	3-Cl	Me	C_6H_5	200	55		
$C_{11}H_{12}ClN_3O_2$	4-Cl	Me	Me	266–268[d]	62	3320, 3280	1670
$C_{14}H_{16}ClN_3O_2$	4-Cl	—$(CH_2)_5$—		256–258	73		
$C_{15}H_{11}ClN_4O_4$	4-Cl	H	2-$NO_2C_6H_4$	292–294	84		
$C_{15}H_{12}ClN_3O_3$	4-Cl	H	2-CHC_6H_4	269–270	85		
$C_{16}H_{14}ClN_3O_2$	4-Cl	Me	C_6H_5	290	76		
$C_{18}H_{16}ClN_3O_2$	4-Cl	Me	C_6H_5CH=CH	259–260	84		
$C_{15}H_{11}Cl_2N_3O_2$	4-Cl	H	2-ClC_6H_4	278	89		
$C_{15}H_{10}Cl_3N_3O_2$	4-Cl	H	3,4-$Cl_2C_6H_3$	281–282	77		
$C_{17}H_{17}N_5O_2$	4-$C_6H_5N_2$	Me	Me	259–260	86	3340, 3300	1670
$C_{17}H_{17}N_3O_2$	3-Me	Me	C_6H_5	192–193	82		
$C_{19}H_{19}N_3O_2$	3-Me	Me	C_6H_5—CH=CH	197	68		
$C_{16}H_{15}N_3O_3$	3-Me	H	2-OHC_6H_4	214–216	90		
$C_{18}H_{17}N_3O_2$	3-Me	H	C_6H_5CH=CH	250–252	65		
$C_{12}H_{15}N_5O_2$	4-Me	Me	Me	200–201	83	3280 br	1680
$C_{16}H_{14}N_4O_4$	4-Me	H	2-$NO_2C_6H_4$	265–266	87		
$C_{15}H_{19}N_3O_3$	4-Me	—$(CH_2)_5$—		199–201	92		
$C_{17}H_{17}N_3O_2$	4-Me	Me	C_6H_5	220	75		
$C_{16}H_{13}Cl_2N_3O_2$	4-Me	H	3,4-$Cl_2C_6H_3$	275–276	93		
$C_{11}H_{12}N_4O_4$	2-NO_2	Me	Me	241	67	3320, 3250	1670
$C_{11}H_{12}N_4O_4$	3-NO_2	Me	Me	250–255	65		
$C_{11}H_{12}N_4O_4$	4-NO_2	Me	Me	243–244 [lit. (*24*) 310]	84	3330, 3260	1670
$C_{14}H_{16}N_4O_4$	3-NO_2	—$(CH_2)_5$—		250	81	3300, 3260	1665
$C_{15}H_{11}N_5O_6$	3-NO_2	H	2-$NO_2C_6H_4$	242	85		
$C_{21}H_{16}N_6O_4$	4-$C_6H_5N_2$	H	2-$NO_2C_6H_4$	263–264	90		
$C_{20}H_{21}N_5O_2$	4-$C_6H_5N_2$	—$(CH_2)_5$—		236–239	82		
$C_{22}H_{19}N_5O_2$	4-$C_6H_5N_2$	Me	C_6H_5	266–268	73		
$C_{12}H_{15}N_3O_3$	2-MeO	Me	Me	125	45	3320, 3270	1670
$C_{15}H_{19}N_3O_3$	2-MeO	—$(CH_2)_5$—		233–234	72		
$C_{16}H_{14}N_4O_5$	2-MeO	H	2-$NO_2C_6H_4$	235–238	86		
$C_{17}H_{17}N_3O_3$	2-MeO	Me	C_6H_5	159–160	65		
$C_{16}H_{13}Cl_2N_3O_2$	2-MeO	3,4-$Cl_2C_6H_3$		208–210	80		
$C_{12}H_{15}N_3O_3$	3-MeO	Me	Me	186–187	76	3360, 3290	1680
$C_{15}H_{19}N_3O_3$	3-MeO	—$(CH_2)_5$—		178	75	3320, 3280	1665
$C_{16}H_{14}N_4O_5$	3-MeO	H	2-$NO_2C_6H_4$	220–221	86		
$C_{17}H_{17}N_3O_3$	3-MeO	Me	C_6H_5	191–192	80		
$C_{12}H_{15}N_3O_3$	4-MeO	Me	Me	220–222	58	3340, 3270	1670
$C_{15}H_{19}N_3O_3$	4-MeO	—$(CH_2)_5$—		196–198	55	3310, 3280	1675
$C_{16}H_{14}N_4O_5$	4-MeO	H	2-$NO_2C_6H_4$	251–252	77		
$C_{17}H_{17}N_3O_3$	4-MeO	Me	C_6H_5	227–228	60		
$C_{17}H_{17}N_3O_2$	2-C_6H_5	Me	Me	161–163	57	3360, 3340	1685
$C_{21}H_{16}N_4O_4$	2-C_6H_5	H	2-$NO_2C_6H_4$	198–199	85		
$C_{21}H_{15}Cl_2N_3O_2$	2-C_6H_5	H	3,4-$Cl_2C_6H_3$	214–215	85		
$C_{18}H_{16}N_4O_5$	2-MeO	H	2-$NO_2C_6H_4CH$=CH	265	70		
$C_{18}H_{16}N_4O_5$	3-MeO	H	2-$NO_2C_6H_4CH$=CH	225	65		
			Other *N*-aryloxamic acid hydrazones[a] R[1]—NHCOCONH—N=CR[2]R[3]				
$C_{10}H_{12}N_4O_2$	2-Pyridyl	Me	Me	146–147	86	3340, 3310	1680
$C_{14}H_{10}Cl_2N_4O_2$	2-Pyridyl	H	3,4-$Cl_2C_6H_3$	221–223	75		
$C_{14}H_{11}N_5O_4$	2-Pyridyl	H	2-$NO_2C_6H_4$	215–216	85	3300, 3200	1670
$C_{13}H_{16}N_4O_2$	2-Pyridyl	—$(CH_2)_4$—		171–172	70		
$C_{14}H_{14}N_4O_2$	3-Quinolyl	Me	Me	232–235	85	3310, 3260	1665
$C_{16}H_{16}N_4O_2$	3-Quinolyl	—$(CH_2)_4$—		235–236	70		
$C_{20}H_{15}N_5O_4$	3-Quinolyl	H	2-$NO_2C_6H_4CH$=CH	270	88		
$C_{18}H_{12}Cl_2N_4O_2$	3-Quinolyl	H	3,4-$Cl_2C_6H_5$	310–312	87		
$C_{11}H_{11}Cl_2N_3O_2$	3,4-$Cl_2C_6H_3$	Me	Me	235–237	73	3340, 3260	1680
$C_{15}H_9Cl_4N_3O_2$	3,4-$Cl_2C_6H_3$	H	3,4-$Cl_2C_6H_3$	250	84		
$C_{14}H_{15}Cl_2N_3O_2$	3,4-$Cl_2C_6H_3$	—$(CH_2)_5$—		219–220			
$C_{11}H_{11}Cl_2N_3O_2$	2,4-$Cl_2C_6H_3$	Me	Me	231–233	62	3280 br	1665
$C_{15}H_{10}Cl_2N_4O_4$	2,4-$Cl_2C_6H_3$	H	2-$NO_2C_6H_4$	250	45		

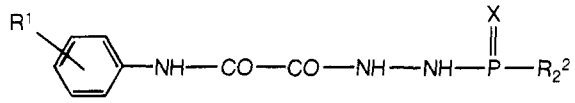
[a] Elemental analyses (C,H,N) in agreement with theoretical values were obtained and submitted for review. Nmr spectra: [b] —0.8 τ (NH, 2), 2.0–2.9 (ArH, 5) doublet 8.0–8.1 τ [$(CH_3)_2C$=]. [c] —0.2 (NH_a), 0.6 (NH_b), 2.0–2.8 (ArH, 4) doublet 7.9–8.1 τ [$(CH_3)_2C$=]. [d] —1.0 (NH, 2), 2.0–2.7 (ArH, 4), doublet 7.9–8.1 τ [$(CH_3)_2C$=].

The *N*-aryloxamic acid hydrazides and their derivatives have been screened for bactericidal, fungicidal, and insecticidal activity. There appeared to be no particular dangers in handling these compounds since they have comparatively low mammalian toxicities.

Experimental

Ir spectra were measured as Nujol mulls with a Perkin-Elmer 257 spectrometer. Nmr spectra were determined with a Varian A60A spectrometer with tetramethylsilane as internal standard; the solvents used were: for the ethyl oxamates, $CDCl_3$; oxamic acid hydrazides, $(CD_3)_2SO$; and for the acetone hydrazones, $CDCl_3$. Melting points were determined with a Kofler Hot-Bench apparatus and are uncorrected. Elemental analyses were performed by Imperial Chemical Industries Ltd., England, and the National Physical Laboratory, Teddington, England. (Elemental analytical results for the compounds have been

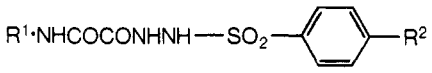
Table IV. *N*-Phosphoryl *N*¹-Aryloxamic Hydrazides[a]



Molecular formula	X	R^1	R^2	Mp, °C	Yield, %	Ir spectra: νN—H, cm^{-1}	νC=O, cm^{-1}	νP=O, cm^{-1}
$C_{22}H_{24}N_5O_3P$	O	H	$C_6H_5CH_2NH$	197–198	35	3350, 3290	1665	1230
$C_{20}H_{18}N_3O_5P$	O	H	C_6H_5O	326–330	54	3340, 3300	1670	1240
$C_{12}H_{18}N_3O_4PS$	S	H	C_2H_5O	202	65	3340, 3300	1670	770, 710 (PS)
$C_{12}H_{18}N_3O_5P$	O	H	C_2H_5O	310–312	26	3320, 3290	1670	1240
$C_{20}H_{20}N_5O_3P$	O	H	C_6H_5NH	198–200	58	3380, 3300	1670	1235
$C_{10}H_{14}N_3O_4PS$	S	H	CH_3O	239–240	40	3340, 3290	1670	771, 710 (PS)
$C_{16}H_{26}N_3O_5P$	O	H	C_4H_9O	278	45	3360, 3280	1675	1240
$C_{12}H_{17}ClN_3O_4PS$	S	4-Cl	C_2H_5O	260–262	51	3360, 3300	1670	170 (PS)
$C_{20}H_{32}N_5O_3P$	O	H	$C_6H_{11}NH$	250	32	3350, 3280	1670	1235
$C_{12}H_{19}ClN_5O_3P$	O	4-Cl	$(CH_3)_2N$	220–222	30	3330, 3290	1730, 1660	1220

[a] Elemental analyses (C,H,N,P) in agreement with theoretical values were obtained and submitted for review.

Table V. *N*-Arylsulfonyl-*N*¹Aryloxamic Acid Hydrazides[a]



Molecular formula	R^1	R^2	Mp, °C	Yield, %	Ir spectra: νN—H, cm^{-1}	νC=O, cm^{-1}	νSO_2, cm^{-1}
$C_{15}H_{14}ClN_3O_4S$	4-ClC_6H_4	Me	210–212	80	3290, 3220	1710, 1675	1350, 1170
$C_{16}H_{17}N_3O_5S$	4-$MeOC_6H_4$	Me	200–201	64	3280, 3200	1660	1350, 1170
$C_{16}H_{17}N_3O_5S$	2-$MeOC_6H_4$	Me	210–212	53	3300, 3200	1705, 1670	1360, 1170
$C_{16}H_{17}N_3O_5S$	3-$MeOC_6H_4$	Me	180–182	86	3360, 3330	1685	1330, 1160
$C_{15}H_{14}ClN_3O_4S$	3-ClC_6H_4	Me	215–216	85	3280, 3220	1710, 1670	1360, 1170
$C_{15}H_{14}ClN_3O_4S$	2-ClC_6H_4	Me	230–231	57	3340, 3260	1730, 1690	1365, 1175
$C_{16}H_{17}N_3O_4S$	3-MeC_6H_4	Me	243–244	50	3310, 3220	1725, 1680	1360, 1170
$C_{16}H_{17}N_3O_4S$	4-MeC_6H_4	Me	226–230	45	3280, 3180	1680, 1660	1350, 1170
$C_{16}H_{17}N_3O_4S$	2-MeC_6H_4	Me	196–197	44	3360, 3230	1680, 1670	1360, 1170
$C_{21}H_{19}N_5O_4S$	4-$C_6H_5N_2$	Me	220	45	3250	1670 br	1170
$C_{15}H_{14}N_4O_6S$	2-$NO_2C_6H_4$	Me	256–258	82	3280, 3220	1700, 1670	1340, 1170
$C_{15}H_{14}N_4O_6S$	3-$NO_2C_6H_4$	Me	264–265	52	3300	1730, 1680	1340, 1170
$C_{15}H_{14}N_4O_6S$	4-$NO_2C_6H_4$	Me	310–311	55	3300	1700 br	1350, 1170
$C_{15}H_{13}Cl_2N_3O_4S$	2,4-$Cl_2C_6H_3$	Me	205	60	3300, 3220	1680	1350, 1170
$C_{15}H_{15}N_3O_4S$	C_6H_5	Me	215–217	70	3280, 3225	1710, 1670	1360, 1170
$C_{21}H_{19}N_3O_4S$	2-Biphenyl	Me	251–252	65	3330, 3240	1730, 1680	1350, 1170
$C_{18}H_{16}N_4O_4S$	3-Quinolyl	Me	282–285	50	2180, 3220	1715, 1670	1360, 1170
$C_{16}H_{16}N_4O_5S$	C_6H_5	AcNH	231–232	42	3290, 3220	1700, 1680	1355, 1170
$C_{16}H_{15}ClN_4O_5S$	4-ClC_6H_4	AcNH	255	60	3300, 3260	1710, 1690	1360, 1170
$C_{17}H_{18}N_4O_6S$	3-$MeOC_6H_4$	AcNH	245–247	75	3350, 3300	1690	1340, 1160
$C_{17}H_{18}N_4O_6S$	4-$MeOC_6H_4$	AcNH	239	70	3280, 3200	1705, 1680	1360, 1170
$C_{17}H_{18}N_4O_6S$	2-$MeOC_6H_4$	AcNH	248–249	82	3300, 3180	1710, 1690	1350, 1160
$C_{16}H_{15}ClN_4O_5S$	3-ClC_6H_4	AcNH	269	85	3280, 3200	1690 br	1360, 1170
$C_{16}H_{15}N_5O_7S$	3-$NO_2C_6H_4$	AcNH	264–265	70	3300 br	1700 br	1350, 1170
$C_{16}H_{14}Cl_2N_4O_5S$	2,4-$Cl_2C_6H_3$	AcNH	265	55	3300, 3225	1680 br	1350, 1170
$C_{22}H_{20}N_4O_5S$	2-Biphenyl	AcNH	263–264	60	3340, 3260	1680	1360, 1175

[a] Elemental analyses (C,H,N) in agreement with theoretical values were obtained and submitted for review.

deposited with the ACS Microfilm Depository Service.)

Substituted ethyl N-aryloxamates (Table I). These were prepared by the standard method (*22*) of heating the appropriate aromatic primary amine with a slight excess of diethyl oxalate for 3–6 hr under reflux to give the compounds listed. The products were crystallized from ethanol or aqueous ethanol. As by-products in the preparation of the ethyl *N*-aryloxamates, substantial amounts of the following new *N,N'*-diaryloxamides (IV) were obtained: 3-pyridyl (IV, R=3-pyridyl), mp 295–298°C; ir 3160 (NHbr), 1690 (C=O) cm^{-1}; 4-pyridyl (IV, R=4-pyridyl), mp 305–307°C; ir 3280 (NHbr), 1690 (C=O) cm^{-1}; 3-quinolyl (IV, R=3-quinolyl), mp 323–325°C; ir 3200 (NHbr), 1685 (C=O) cm^{-1}; and *p*-phenylazo (IV, R=*p*-phenylazo), mp 300–305°C; ir 3340 (NH), 1705, 1680 (C=O) cm^{-1}.

Reaction of 2-aminopyridine with diethyl oxalate. 2-Aminopyridine (28.2 grams) was refluxed with diethyl oxalate (52.5 grams; 1.2 mol equiv) for 6 hr. The mixture was cooled, and the solid product extracted with boiling ethanol to give *N,N'*-di(2-pyridyl)oxamide (IV, R=2-pyridyl) (16.5 grams, 27%), mp 165–167°C [lit. (*15*), mp 161°C]; ir 3310 (NH), 1685 (C=O) cm^{-1}.

When the reaction was repeated by using 2-aminopyridine (18.6 grams) with diethyl oxalate (87.6 grams; 3 mol equiv), cooling gave the dipyridyloxamide (IV) (11.5 grams, 25%), mp 166–167°C. The filtrate, by concentration in vacuo, afforded ethyl *N*-2-pyridyloxamate (16.5 grams, Table I).

N-Aryloxamic acid hydrazides (Table II). These were obtained by portionwise addition of the appropriate ethyl *N*-aryloxamate to an excess of hydrazine hydrate (3 mol equiv) in warm ethanol for 3 hr. On cooling, the products precipitated out, and they were generally recrystallized from ethanol or methanol.

N-Aryloxamic acid hydrazones (Table III). These were generally prepared by heating equimolar amounts of the hydrazide and the carbonyl compound in warm ethanol for 2–3 hr; in some cases, a crystal of iodine was added to accelerate the condensation. On cooling, the products precipitated out, and they were crystallized from ethanol, aqueous ethanol, ethanol–dimethylsulfoxide, or ethanol–dimethylformamide.

N-Phosphoryl-N'-aryloxanilic hydrazides (Table IV). The *N*-aryl oxanilic acid hydrazide was treated with the appropriate phosphorochloridate (1 mol equiv) in pyridine overnight. (If complete solution was not attained, some dimethylsulfoxide was added). The pyridine was removed in vacuo, and the products precipitated by addition of ice water. The products were washed with water and recrystallized from ethanol or ethanol–dimethylformamide.

N-Arylsulfonyl-N'-aryloxamic hydrazides (Table V). These were similarly prepared by condensation of the oxamic acid hydrazide with *p*-toluenesulfonyl chloride or N^4-acetylsulfanilyl chloride in pyridine overnight. The products were recrystallized from ethanol or ethanol–acetonitrile.

N,N-Dimethylcarbamoyl-N'-aryloxamic hydrazides (Table VI). These were obtained by reaction of the oxamic acid hydrazide with *N,N*-dimethylcarbamoyl chloride–pyridine overnight. The products were recrystallized from ethanol or ethanol–dimethylformamide.

N-Ethoxycarbonyl derivatives (Table VI). These were obtained by reaction of the hydrazide with ethyl chloroformate–pyridine overnight. The products were recrystallized from ethanol or ethanol–dimethylformamide.

Reaction of N,N'-di(2-pyridyl)oxamide with hydrazine hydrate. *Large excess of hydrazine.* The oxamide (1.2 grams) was boiled with 99% hydrazine hydrate (1 ml, 4 mol equiv) in ethanol (10 ml) for 3 hr to give oxalic acid dihydrazide (0.8 gram), mp 242–244°C [lit. (*10*), mp 240–242°C]; ir 3280, 3180 (NH), 1675 (CO br) cm^{-1}. Identity of product was confirmed by preparation of the di-3,4-dichlorobenzaldehyde dihydrazone as plates, mp 300°C.

Less hydrazine. The oxamide (1.2 grams) was treated with hydrazine hydrate (0.5 gram, 2 mol equiv) in ethanol (20 ml) for 2 hr to give *N*-2-pyridyl-oxamic acid hydrazide (0.4 gram), mp 196–198° [lit. (*20*), mp 300°C.]

The structure was confirmed by preparation of the acetone and 3,4-dichlorobenzaldehyde hydrazones which were identical (ir and mp) to the similar derivatives

Table VI. *N,N*-Dimethylcarbamoyl *N*-Aryloxamic Acid Hydrazides[a]

R—NH·CO·CO·NH·NHCONMe$_2$

Molecular formula	R	Mp, °C	Solvent for crystallization	Yield, %	Ir spectra	
					νN—H, cm^{-1}	νC=O, cm^{-1}
$C_{11}H_{14}N_4O_3$	C_6H_5	195–197	EtOH–DMF[b]	45	3340, 3310	1690, 1670
$C_{12}H_{16}N_4O_4$	3-$MeOC_6H_4$	193–194	EtOH–DMF	40	3330, 3290	1685, 1670
$C_{12}H_{16}N_4O_4$	4-$MeOC_6H_4$	210–212	aq MeOH	35	3340, 3300	1680, 1670
$C_{12}H_{16}N_4O_3$	4-MeC_6H_4	217–218	EtOH–DMSO[c]	30	3280, 3220	1675, 1650
$C_{11}H_{13}ClN_4O_3$	4-ClC_6H_4	195–196	EtOH–DMSO	65	3340, 3260	1680, 1660
$C_{11}H_{13}ClN_4O_3$	3-ClC_6H_4	205	aq EtOH	56	3280, 3240	1685, 1650
$C_{17}H_{18}N_4O_3$	2-Biphenyl	183–184	EtOH–MeCN	65	3330, 3260	1685, 1650
$C_{11}H_{12}Cl_2N_4O_3$	3,4-$Cl_2C_6H_3$	200	EtOH–DMSO	70	3290 br	1685, 1650
$C_{14}H_{15}N_5O_3$	3-Quinolyl	255–256	aq MeOH	65	3340, 3280	1690, 1665
		N-Ethoxycarbonyl *N*-aryloxamic acid hydrazides[a] R—NHCOCONH—$NHCO_2Et$				
$C_{11}H_{18}N_3O_4$	C_6H_5	250	EtOH–DMF	50	3290 br	1730, 1660
$C_{11}H_{12}ClN_3O_4$	4-ClC_6H_4	333–335	EtOH–DMSO	55	3270	1725, 1655
$C_{12}H_{15}N_3O_5$	4-$MeOC_6H_4$	193	MeOH–Me_2CO	70	3280	1730, 1655
$C_{11}H_{12}ClN_3O_4$	3-ClC_6H_4	210–211	EtOH–DMF	60	3280	1725, 1660
$C_{11}H_{11}Cl_2N_3O_4$	3,4-$Cl_2C_6H_3$	218–221	EtOH–DMSO	50	3280	1730, 1670
$C_{11}H_{12}N_4O_6$	3-$NO_2C_6H_4$	190	EtOH–Me_2CO	45	3280	1730, 1680

[a] Elemental analyses (C,H,N) in agreement with theoretical values were obtained and submitted for review. [b] DMF = dimethylformamide. [c] DMSO = dimethylsulfoxide.

(Table III) from the authentic hydrazide obtained from ethyl *N*-(2-pyridyl)oxamate.

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Supplementary Material Available. Eleven pages of elemental analytical results for the compounds will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-288.

Benzenesulfonamides of Primary Aminopyridines and Primary Aminoquinolines

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Sulfonamides of 12 aminopyridines and aminoquinolines are prepared. For the preparation of these sulfonamides, pyridine is a more suitable solvent than acetic acid.

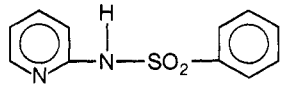
The preparation of sulfonamides of primary and secondary amines is a well-known avenue to the classification and identification of such compounds. However, the benzenesulfonamides of a number of common aminopyridines and aminoquinolines have not been reported. Twelve such sulfonamides are described here. Since the completion of this work, three of the derivatives have been reported with melting points in substantial agreement with our data. They are indicated in Table I.

Various modifications of the original Hinsberg method have been suggested. The ones cited here (*1, 6, 7, 10, 11, 13*) all use nonaqueous solvents. The variants used by Mills and Breckenridge (*7*) and Shepherd (*11*) were the basis of the present study. The former used pyridine as the solvent, whereas Shepherd used glacial acetic acid, with sodium acetate as catalyst. While interpreting the reaction in relation to amine basicity, Shepherd suggested that the pyridine method might be improved by adding triethylamine in certain cases.

Published procedures involve washing the product with acid to remove the substrate. In the present cases the products themselves are also basic, and the acid wash is inadvisable. However, simple recrystallization from diluted ethanol sufficed to produce the pure derivative in one to three recrystallizations.

In addition to the new cases shown in Table I, we found that 2-aminopyridine, 2-amino-3-methylpyridine, and 2-amino-5-methylpyridine failed to produce the sulfonamide in glacial acetic acid, and 8-aminoquinoline gave 92% of crude product in the acid solvent. Table I shows that, with 3-aminopyridine and 3-aminoquinoline, the acetic acid method gave lower yields, and it failed entirely with four others. On the other hand, with 4-aminoquinaldine, the pyridine methods (B and C) gave only intractable oils, and the acid method (A) gave 59% of derivative. Thus, in general, the observations of Winterbottom (*14*) are supported; namely, that acetic acid is inferior to pyridine or entirely unsuitable as a solvent for 2- and 4-aminopyridines.

The precise structure of similar derivatives of certain 2- and 4-amino-substituted pyridines has been studied (*2, 3, 5, 12*). Whether structure I or II applies in these cases is not debated here. In the cases of the monosulfonamides reported here, the products are those obtained by the methods indicated, and are suitable for identification



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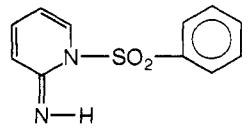

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