Journal of Crystallographic and Spectroscopic Research, Vol. 18, No. 2, 1988

Crystallographic study of restricted rotation in *o*-formanilides

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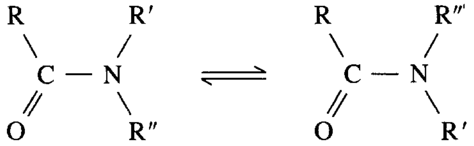
(*Received October 25, 1987*)

Abstract

The crystal structures of *cis*- and *trans-o*-methylformanilide, of its *cis*-thio analogue, and of *trans-o*-phenylformanilide have been studied with a view to clarifying the anomalously high barrier to rotation of the carbonyl group. The pair of resolved geometrical isomers is shown to be stabilized in the solid state primarily by hydrogen bonding. The increased barrier to rotation is inferred not to arise from mesomeric involvement of the carbonyl group, but from nuclear screening by the nitrogen lone pair.

Introduction

An anomalously high barrier to rotation around the C–N single bond is observed for simple amides. It arises from electronic and steric factors and is often complicated by hydrogen bonding. In the simplest form of a substituted formamide, the amide has a planar skeleton:

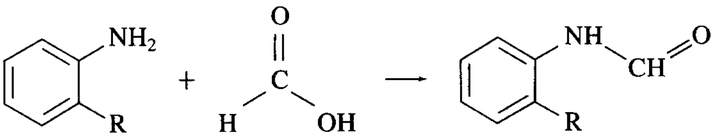


A lower limit for the barrier to rotation, as derived from the temperature dependence of magnetic nonequivalence, appears to be about 40 kJ mol^{-1} (Kessler, 1970). This is sufficient to produce rotational isomers in both the solid state and in solution (Domiano, *et al.*, 1986).

Pure *cis* and *trans* rotamers of *o*-methylformanilides were first isolated in the solid state by Siddall *et al.* (1968). The structures of these rotamers, of the *trans* isomer of the sulfur analogue, and of *o*-phenylformanilide are described in this paper. It was not possible to isolate the Z isomer of the sulfur analogue, despite evidence that replacement of the amide oxygen by sulfur or selenium increases the rotational barrier by as much as 20 kJ mol^{-1} (Stewart and Siddall, 1970). The phenyl derivative has only been obtained as the *Z* isomer.

Experimental

o-Methylformanilide (**1**, $R = CH_3$) and *o*-phenylformanilide (**3**) were obtained by distilling off excess formic acid from a reaction mixture (Siddall *et al.*, 1968):



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The thio analogue (**2**) was prepared by treatment of **1** with P_2S_5 in benzene and separated on a column. Crystals from the leading fraction in ethyl acetate–hexane were used directly without recrystallization. Recrystallization of **1** afforded large, rectangular plates of one isomer (*t*-**1**) together with agglomerates of very small platelike crystals (*c*-**1**), readily distinguished from the former under the microscope. Repeated efforts to produce two rotamers of **2** were unsuccessful. Only the *cis* isomer was obtained. These assignments follow the notation of Siddall *et al* (1968).

Single crystals were sealed into Lindemann capillaries for preliminary oscillation and Weissenberg photography, and detailed examination on a Nonius CAD4 single-crystal diffractometer, with an incident-beam graphite-crystal monochromator. Cell constants were obtained from least-squares refinement of 25 accurately measured high-angle θ values. Crystal data and details of the structure analyses are summarized in Table 1. Intensity scan parameters were determined according to standard CAD4 procedures. Intensity checks on three standards were performed each hour to monitor crystal decay. Data reduction consisted of correction for background, Lorentz and polarization factors, and absorption by the empirical method of North *et al* (1968), from azimuthal scans

Table 1. Crystal data and details of the structure analysis

	c-**1**	*t*-**1**	*c*-**2**	*t*-**3**
Compound formula	C_8H_9NO	C_8H_9NO	C_8H_9NS	$C_{13}H_{11}NO$
M_r	135.17	135.17	151.23	197.24
Space Group	$P2_1/c$	$P2_1/c$	*Pccn*	$P2_1$
a (Å)	7.077(1)	12.778(3)	15.381(3)	7.072(1)
b (Å)	13.388(2)	8.315(3)	13.651(1)	7.509(4)
c (Å)	7.933(1)	7.093(1)	7.839(9)	10.206(2)
β (deg)	100.01(1)	100.48(1)	—	91.15(1)
V_c (Å^3)	740.21	741.05	1645.92	541.87
Z	4	4	8	2
D_c (gh cm^{-3})	1.21	1.21	1.22	1.21
F(000)	288	288	640	208
μ (Mo $K\alpha$) (cm^{-1})	0.47	0.47	2.71	0.43
Scan range (deg)	$3 \le \theta \le 30$	$3 \le \theta \le 30$	$3 \le \theta \le 30$	$3 \le \theta \le 30$
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
h	−9–9	−10–10	0–21	−9–9
k	0–18	0–11	0–19	0–9
l	0–11	0–18	0–11	0–13
I(obs)	724	795	1514	768
Cut-off	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 4\sigma(F)$	$F > \sigma(F)$
LS parameters	127	92	127	136
Max. Δ/σ	0.01	0.001	0.05	0.01
Residual density (e Å^{-3})	0.22	0.34	0.30	0.44
R	0.066	0.11	0.045	0.14
R_w	0.043	0.09	—	0.052
Weighting scheme, *w*	$1/\sigma^2(F)$	$1/\sigma^2(F)$	unity	$1/\sigma^2(F)$

of nine suitable reflections in 37 different orientations, at 10° intervals, around the diffraction vector.

The structures were solved using the direct-methods package of SHELXS 86 (Sheldrick, 1985), and refined by full-matrix least squares, using SHELX 76 (Sheldrick, 1976). The hydrogen atoms of *c*-**1** and *c*-**2** were located by difference Fourier methods, but those of *t*-**1** and **3** were placed at geometrically calculated positions. All nonhydrogen atoms were refined anisotropically. The structure of *t*-**1**, for no apparent reason, refined not as well as *c*-**1** and *c*-**2**. The poor fit obtained for **3** is due to low-quality crystal and data.

The refined coordinates are listed in Tables 2–5 according to the numbering schemes shown in Fig. 1, which represents the molecular structures as stereo pairs.

Table 2. Fractional coordinates (× 10^4) and equivalent isotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of *c*-**1**

	x	*y*	*z*	*U*(eq)
O	2404(3)	−400(2)	20(5)	71(1)
N	1444(4)	1213(2)	−41(5)	48(1)
C(1)	1865(5)	2255(2)	30(6)	45(1)
C(2)	570(5)	2916(3)	−898(6)	47(1)
C(3)	1061(6)	3923(3)	−822(6)	58(1)
C(4)	2763(6)	4253(3)	135(8)	68(1)
C(5)	4017(6)	3589(3)	1043(7)	65(1)
C(6)	3559(5)	2589(3)	1011(6)	54(1)
C(7)	−1290(6)	2569(4)	−1938(8)	60(1)
C(8)	2755(5)	486(3)	−4(7)	61(1)

Anisotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of *c*-**1**

	U(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
O	42(2)	39(1)	133(3)	1(2)	10(2)	1(1)
N	29(2)	44(2)	70(3)	2(2)	3(2)	−4(2)
C(1)	38(2)	44(2)	53(3)	−2(2)	14(2)	−1(2)
C(2)	40(2)	50(3)	50(4)	1(2)	11(2)	3(2)
C(3)	53(3)	48(3)	72(4)	10(3)	15(3)	12(2)
C(4)	65(3)	43(3)	97(5)	−6(3)	24(3)	−10(2)
C(5)	49(3)	59(3)	86(4)	−8(3)	3(3)	−12(2)
C(6)	39(2)	51(3)	72(4)	5(3)	−3(2)	−1(2)
C(7)	45(2)	64(3)	71(4)	7(4)	−8(3)	1(3)
C(8)	35(3)	57(3)	90(4)	−2(3)	11(3)	3(2)

Fractional coordinates (× 10^3) and common isotropic temperature factors (Å^2, × 10^2) for hydrogen atoms of *c*-**1**

	x	*y*	*z*	*U*
H	39(4)	101(2)	−12(5)	4(1)
H(3)	10(4)	439(2)	−147(4)	6(1)
H(4)	310(4)	497(3)	12(5)	7(1)
H(5)	523(5)	383(2)	176(5)	7(1)
H(6)	440(4)	210(2)	176(4)	5(1)
H(71)	−221(5)	229(3)	−123(6)	9(2)
H(72)	−117(5)	200(3)	−271(5)	8(2)
H(73)	−191(5)	310(3)	−261(5)	8(2)
H(8)	421(4)	75(2)	−13(5)	6(1)

Bond lengths (Å) and angles (deg) of *c*-**1**

O-C(8)	1.213(4)	N-C(1)	1.426(4)
N-C(8)	1.342(4)	C(1)-C(2)	1.390(4)
C(1)-C(6)	1.386(4)	C(2)-C(3)	1.390(5)
C(2)-C(7)	1.501(5)	C(3)-C(4)	1.380(5)
C(4)-C(5)	1.369(5)	C(5)-C(6)	1.376(5)
C(1)-N-C(8)	124.7(3)	N-C(1)-C(2)	119.2(3)
N-C(1)-C(6)	119.5(3)	C(2)-C(1)-C(6)	121.2(3)
C(1)-C(2)-C(3)	117.2(3)	C(1)-C(2)-C(7)	121.9(4)
C(3)-C(2)-C(7)	120.9(4)	C(2)-C(3)-C(4)	121.5(4)

Table 2. Continued

	x	*y*	*z*	*U*
	Bond lengths (Å) and angles (deg) of *c*-**1**			
C(3)-C(4)-C(5)	120.3(4)		C(4)-C(5)-C(6)	119.6(4)
C(1)-C(6)-C(5)	120.1(4)		O-C(8)-N	124.5(4)
	Bond lengths (Å) involving hydrogen atoms for *c*-**1**			
N-H	0.79(3)		C(3)-H(3)	0.99(3)
C(4)-H(4)	0.99(3)		C(5)-H(5)	1.00(3)
C(6)-H(6)	1.01(3)		C(7)-H(71)	1.01(4)
C(7)-H(72)	0.99(4)		C(7)-H(73)	0.95(4)
C(8)-H(8)	1.11(3)			

Table 3. Fractional coordinates (× 10^4) and equivalent isotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of *t*-**1**

	x	*y*	*z*	*U*(eq)
O	4711(5)	2770(8)	3707(8)	64(2)
N	4108(5)	275(9)	2603(9)	51(2)
C(1)	3010(6)	399(11)	2801(11)	48(2)
C(2)	2263(7)	−395(11)	1440(12)	55(2)
C(3)	1206(7)	−364(12)	1714(13)	68(3)
C(4)	896(7)	427(13)	3199(14)	78(3)
C(5)	1644(8)	1193(13)	4521(13)	81(3)
C(6)	2724(7)	1180(11)	4344(12)	62(3)
C(7)	2556(7)	−1218(13)	−286(12)	90(3)
C(8)	4830(7)	1477(12)	3047(11)	53(2)

Anisotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of *t*-**1**

	U(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
O	69(4)	56(4)	69(4)	−9(3)	23(3)	−23(4)
N	50(4)	55(5)	49(4)	3(4)	16(4)	1(4)
C(1)	42(5)	56(6)	45(5)	−5(5)	10(4)	−2(5)
C(2)	58(6)	58(6)	50(5)	−4(5)	7(5)	−1(5)
C(3)	54(6)	81(7)	70(7)	1(6)	−1(5)	−7(6)
C(4)	49(6)	100(9)	87(8)	−11(7)	23(6)	−16(6)
C(5)	64(7)	107(8)	73(7)	−9(7)	37(6)	3(7)
C(6)	53(6)	82(7)	50(5)	−6(5)	20(4)	−2(5)
C(7)	75(7)	131(10)	64(6)	−45(7)	3(6)	6(7)
C(8)	52(6)	67(6)	40(5)	9(5)	14(4)	−7(6)

Fractional coordinates (× 10^4) and common isotropic temperature factors (Å^2, × 10^3) for hydrogen atoms of *t*-**1**

	x	*y*	*z*	*U*
H	4374(5)	−841(9)	2069(9)	187(18)
H(3)	612(7)	−993(12)	704(13)	187(18)

Table 3. Continued

	x	y	z	U
H(4)	68(7)	450(13)	3332(14)	187(18)
H(5)	1404(8)	1814(13)	5710(13)	187(18)
H(6)	3317(7)	1770(11)	5398(12)	187(18)
H(71)	3403(7)	−1112(13)	−240(12)	187(18)
H(72)	2134(7)	−657(13)	−1577(12)	187(18)
H(73)	2340(7)	−2474(13)	−279(12)	187(18)
H(8)	5617(7)	1230(12)	2766(11)	187(18)
		Bond lengths (Å) and angles (deg) of *t*-**1**		
O-C(8)	1.194(9)		N-C(1)	1.439(9)
N-C(8)	1.358(10)		C(1)-C(2)	1.394(10)
C(1)-C(6)	1.378(10)		C(2)-C(3)	1.399(12)
C(2)-C(7)	1.508(11)		C(3)-C(4)	1.361(12)
C(4)-C(5)	1.368(12)		C(5)-C(6)	1.409(11)
C(1)-N-C(8)	123.9(8)		N-C(1)-C(2)	117.1(7)
N-C(1)-C(6)	121.0(7)		C(2)-C(1)-C(6)	121.8(7)
C(1)-C(2)-C(3)	116.8(8)		C(1)-C(2)-C(7)	122.5(8)
C(3)-C(2)-C(7)	120.6(9)		C(2)-C(3)-C(4)	122.8(9)
C(3)-C(4)-C(5)	119.4(8)		C(4)-C(5)-C(6)	120.6(9)
C(1)-C(6)-C(5)	118.7(8)		O-C(8)-N	128.6(8)
		Bond lengths (Å) involving hydrogen atoms for *t*-**1**		
N-H	1.080(0)		C(3)-H(3)	1.080(0)
C(4)-H(4)	1.080(0)		C(5)-H(5)	1.080(0)
C(6)-H(6)	1.080(0)		C(7)-H(71)	1.080(0)
C(7)-H(72)	1.080(0)		C(7)-H(73)	1.080(0)
C(8)-H(8)	1.080(0)			

Table 4. Fractional coordinates (× 10^4) and equivalent isotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of **2**

	x	y	z	U(eq)
S	3691(1)	1917(1)	−27(1)	57(1)
N	3650(2)	3815(2)	741(3)	42(1)
C(1)	3605(2)	4828(2)	329(3)	41(1)
C(2)	4085(2)	5501(2)	1280(3)	43(1)
C(3)	4053(2)	6481(2)	786(4)	56(1)
C(4)	3549(3)	6774(3)	−613(5)	69(1)
C(5)	3074(3)	6100(3)	−1514(5)	69(1)
C(6)	3089(2)	5127(2)	−1053(4)	56(1)
C(7)	4630(3)	5202(3)	2773(5)	63(1)
C(8)	3630(2)	3100(2)	−402(3)	46(1)

Table 4. Continued

Anisotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of **2**

	U(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
S	92(1)	43(1)	35(1)	−4(1)	−7(1)	7(1)
N	58(1)	41(1)	28(1)	0(1)	−6(1)	0(1)
C(1)	47(1)	41(1)	34(1)	0(1)	3(1)	1(1)
C(2)	49(2)	47(1)	34(1)	−2(1)	5(1)	−4(1)
C(3)	65(2)	47(2)	56(2)	−4(1)	14(2)	−7(1)
C(4)	84(3)	49(2)	74(2)	19(2)	13(2)	9(2)
C(5)	76(2)	65(2)	65(2)	18(2)	−12(2)	11(2)
C(6)	61(2)	55(2)	51(2)	5(1)	−14(2)	2(2)
C(7)	78(3)	67(2)	44(2)	2(2)	−14(2)	−22(2)
C(8)	62(2)	47(1)	30(1)	−2(1)	−4(1)	3(1)

Fractional coordinates (× 10^3) and common isotropic temperature factors (Å^2, × 10^3) for hydrogen atoms of **2**

	x	*y*	*z*	*U*
H	373(2)	368(2)	161(4)	73(12)
H(3)	451(2)	696(2)	141(4)	74(10)
H(4)	348(2)	745(3)	−92(4)	84(11)
H(5)	265(2)	632(2)	−235(5)	93(13)
H(6)	269(2)	463(2)	−160(4)	57(9)
H(71)	501(2)	576(3)	305(5)	88(12)
H(72)	439(2)	501(3)	340(4)	67(14)
H(73)	502(2)	457(3)	254(5)	89(12)
H(8)	340(3)	335(3)	−156(5)	114(14)

Bond lengths (Å) and angles (deg) of **2**

S-C(8)	1.645(3)	N-C(1)	1.422(3)
N-C(8)	1.325(3)	C(1)-C(2)	1.393(4)
C(1)-C(6)	1.404(4)	C(2)-C(3)	1.393(4)
C(2)-C(7)	1.496(4)	C(3)-C(4)	1.401(5)
C(4)-C(5)	1.371(5)	C(5)-C(6)	1.377(4)
C(1)-N-C(8)	124.2(2)	N-C(1)-C(2)	119.6(2)
N-C(1)-C(6)	119.0(2)	C(2)-C(1)-C(6)	121.4(2)
C(1)-C(2)-C(3)	117.7(3)	C(1)-C(2)-C(7)	122.4(3)
C(3)-C(2)-C(7)	119.9(3)	C(2)-C(3)-C(4)	120.8(3)
C(3)-C(4)-C(5)	120.4(3)	C(4)-C(5)-C(6)	120.2(3)
C(1)-C(6)-C(5)	119.5(3)	S-C(8)-N	126.9(2)

Bond lengths (Å) involving hydrogen atoms for **2**

N-H	0.72(3)	C(1)-H	1.87(3)
C(2)-H(72)	1.85(4)	C(3)-H(3)	1.09(3)
C(4)-H(4)	0.95(4)	C(5)-H(5)	0.97(4)
C(6)-H(6)	1.01(3)	C(7)-H(71)	0.99(4)
C(7)-H(72)	0.67(3)	C(7)-H(73)	1.07(4)
C(8)-H	1.77(3)	C(8)-H(8)	1.03(4)
H(71)-H(72)	1.43(5)	H(72)-H(73)	1.32(5)

Table 5. Fractional coordinates (× 10^4) and equivalent isotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of **3**

	x	*y*	*z*	*U*(eq)
O	6319(8)	2791	9497(5)	61(2)
N	4401(7)	4989(11)	8685(5)	40(2)
C(1)	3872(12)	4322(14)	7432(7)	44(2)
C(2)	2303(11)	5173(14)	6816(8)	45(3)
C(3)	1737(10)	4576(15)	5577(9)	57(3)
C(4)	2697(12)	3139(15)	4990(8)	60(3)
C(5)	4248(11)	2352(15)	5596(8)	62(3)
C(6)	4851(10)	2943(16)	6824(7)	47(2)
C(7)	1299(10)	6629(13)	7415(8)	34(2)
C(8)	1825(11)	8402(14)	7137(7)	48(2)
C(9)	852(12)	9832(14)	7674(8)	64(3)
C(10)	−620(11)	9497(17)	8515(9)	61(3)
C(11)	−1106(11)	7803(18)	8803(8)	71(3)
C(12)	−161(12)	6348(14)	8284(8)	51(2)
C(13)	5485(11)	4218(12)	9581(9)	54(3)

Anisotropic temperature factors (Å^2, × 10^3) for nonhydrogen atoms of **3**

	U(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
O	61(4)	65(4)	56(4)	15(4)	−12(3)	21(4)
N	44(4)	41(4)	36(4)	−2(4)	−7(3)	12(4)
C(1)	56(6)	38(6)	40(5)	−3(5)	7(5)	1(5)
C(2)	49(6)	37(6)	49(7)	12(6)	2(5)	−13(5)
C(3)	39(5)	76(8)	56(7)	−11(6)	−10(5)	1(6)
C(4)	68(7)	71(7)	42(5)	−10(6)	−8(5)	−13(7)
C(5)	79(8)	56(7)	50(6)	−19(5)	36(5)	−11(5)
C(6)	42(6)	55(6)	45(5)	6(6)	6(5)	12(6)
C(7)	26(5)	48(5)	29(5)	−10(5)	−12(4)	8(5)
C(8)	51(6)	47(6)	47(5)	4(6)	−2(4)	0(5)
C(9)	80(7)	52(6)	58(6)	−16(6)	−9(6)	18(7)
C(10)	51(6)	76(8)	56(6)	−13(6)	−8(5)	15(7)
C(11)	60(6)	71(8)	83(7)	−4(8)	26(5)	6(6)
C(12)	47(5)	50(6)	56(6)	7(5)	10(5)	−7(5)
C(13)	47(6)	62(7)	52(6)	7(6)	11(5)	−3(6)

Fractional coordinates (× 10^4) and common isotropic temperature factors (Å^2, × 10^3) for hydrogen atoms of **3**

	x	*y*	*z*	*U*
H	3849(7)	6284(11)	8934(5)	88(8)
H(3)	566(10)	5209(15)	5066(9)	88(8)
H(4)	2207(12)	2646(15)	4048(8)	88(8)
H(5)	4988(11)	1283(15)	5117(8)	88(8)
H(6)	6066(10)	2342(16)	7305(7)	88(8)
H(8)	2996(11)	8653(14)	6499(7)	88(8)
H(9)	1240(12)	11183(14)	7438(8)	88(8)
H(10)	−1381(11)	10593(17)	8942(9)	88(8)
H(11)	−2264(11)	7572(18)	9455(8)	88(8)

Table 5. Continued

	x	*y*	*z*	*U*
H(12)	−558(12)	5010(14)	8555(8)	88(8)
H(13)	5662(11)	4923(12)	10497(9)	88(8)

Bond lengths (Å) and angles (deg) of **3**

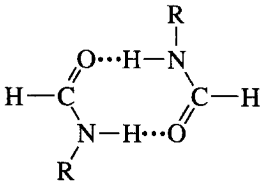
O-C(13)	1.227(8)	N-C(1)	1.417(7)
N-C(13)	1.316(9)	C(1)-C(2)	1.417(9)
C(1)-C(6)	1.398(9)	C(2)-C(3)	1.392(9)
C(2)-C(7)	1.446(10)	C(3)-C(4)	1.415(11)
C(4)-C(5)	1.381(9)	C(5)-C(6)	1.389(9)
C(7)-C(8)	1.413(10)	C(7)-C(12)	1.391(9)
C(8)-C(9)	1.394(9)	C(9)-C(10)	1.385(10)
C(10)-C(11)	1.351(11)	C(11)-C(12)	1.391(11)
C(1)-N-C(13)	127.7(7)	N-C(1)-C(2)	115.6(7)
N-C(1)-C(6)	122.6(8)	C(2)-C(1)-C(6)	121.8(7)
C(1)-C(2)-C(3)	117.8(8)	C(1)-C(2)-C(7)	122.7(7)
C(3)-C(2)-C(7)	119.5(8)	C(2)-C(3)-C(4)	119.9(9)
C(3)-C(4)-C(5)	121.3(9)	C(4)-C(5)-C(6)	119.6(8)
C(1)-C(6)-C(5)	119.4(8)	C(2)-C(7)-C(8)	119.6(7)
C(2)-C(7)-C(12)	122.2(8)	C(8)-C(7)-C(12)	118.2(7)
C(7)-C(8)-C(9)	120.8(7)	C(8)-C(9)-C(10)	119.2(9)
C(9)-C(10)-C(11)	120.2(9)	C(10)-C(11)-C(12)	122.1(8)
C(7)-C(12)-C(11)	119.5(8)	O-C(13)-N	127.6(9)

Bond lengths (Å) involving hydrogen atoms for **3**

N-H	1.080(0)	C(3)-H(3)	1.080(0)
C(4)-H(4)	1.080(0)	C(5)-H(5)	1.080(0)
C(6)-H(6)	1.080(0)	C(8)-H(8)	1.080(0)
C(9)-H(9)	1.080(0)	C(10)-H(10)	1.080(0)
C(11)-H(11)	1.080(0)	C(12)-H(12)	1.080(0)
C(13)-H(13)	1.080(0)		

Discussion

The two methylformanilide structures probably represent the first example of crystallographically characterized rotamers of simple monosubstituted amines. The rotamers exist, not just because of restricted rotation around the C–N bond, but mainly because of hydrogen-bond stabilization. The hydrogen bonding is clearly obvious in the packing diagrams shown in Figs. 2 and 3. The *cis* rotamer occurs as centrosymmetrically hydrogen-bonded dimers of the type



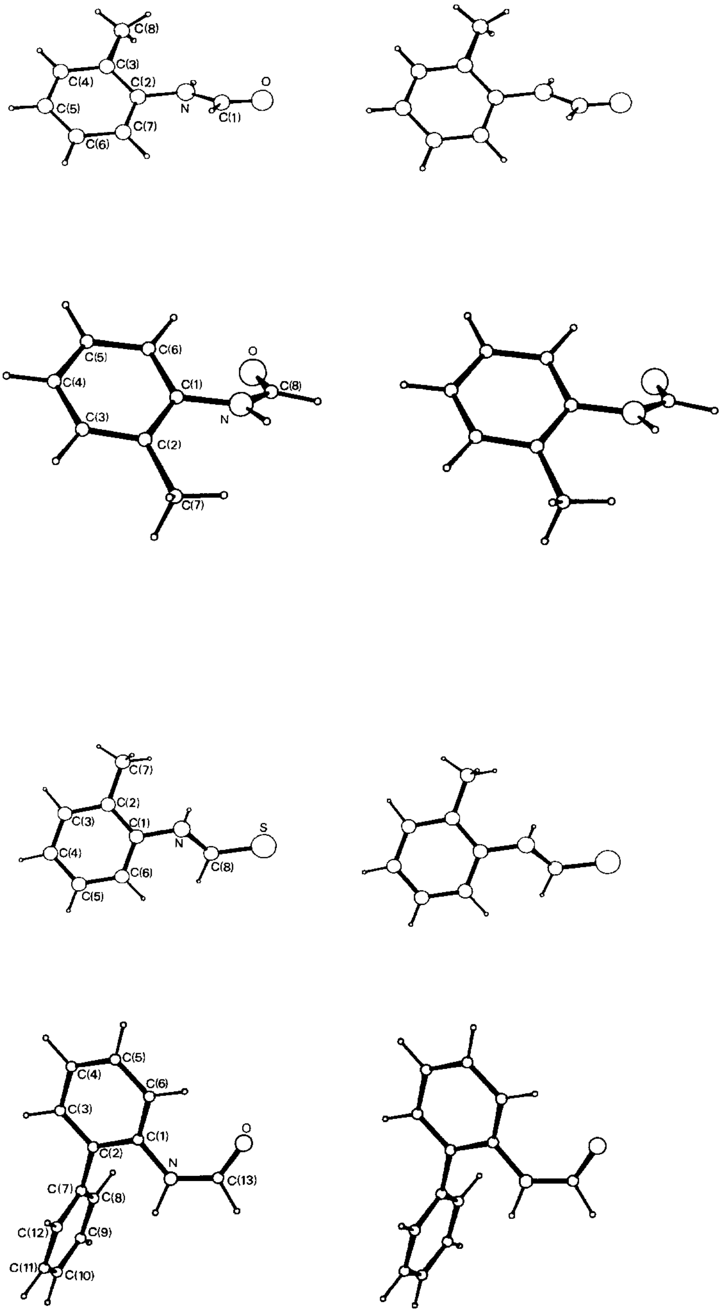


Fig. 1. Stereoscopic drawings of the molecular structures of *c*-**1**, *t*-**1**, **2**, and **3** respectively, showing the crystallographic atomic numbering schemes.

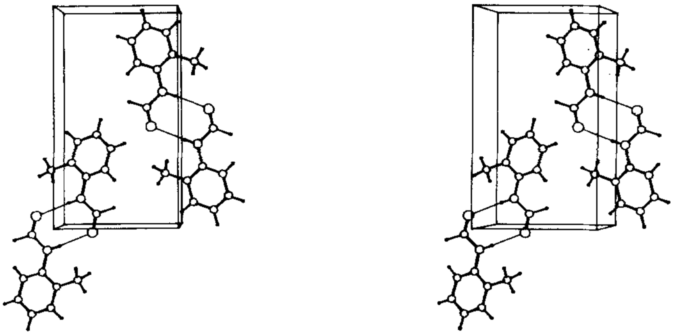
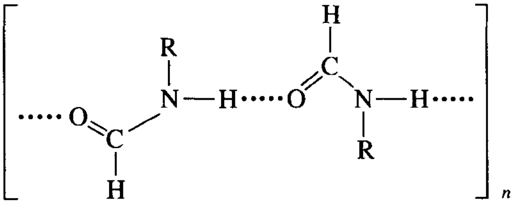
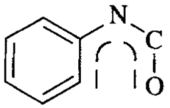


Fig. 2. Stereoscopic packing diagram of *c*-**1** to illustrate the hydrogen bonding.

whereas the *trans* rotamer forms linear hydrogen-bonded chains



This obscures the issue of restricted rotation, supposed to result from delocalization which couples the amide group to the aromatic system to yield a planar arrangement such as



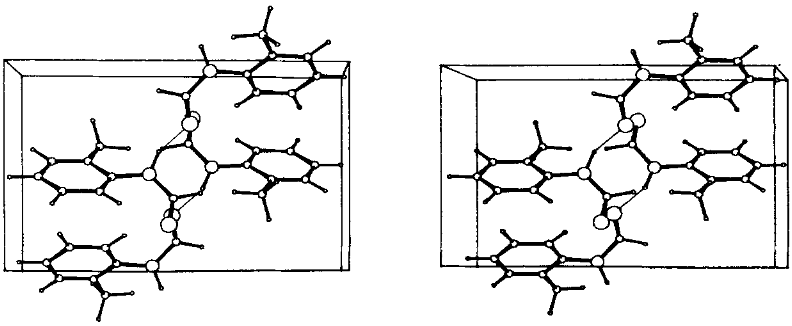
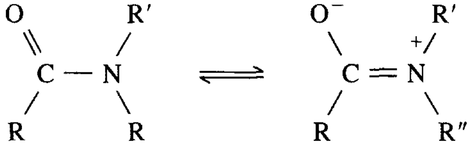


Fig. 3. Stereoscopic packing diagram of *t*-**1** to illustrate the hydrogen bonding.

The torsion angle around the C–N bond, in both the *cis* and *trans* rotamers [2.6(9) and 176.2(9)° respectively], is consistent with this scheme, but the amide group does not line up with the aromatic plane. The corresponding torsion angles of type C(2)–C(1)–N–C(8) are 145(1)° in both structures. Despite this non-planarity, appreciable conjugation seems to be implied by the partial double-bond character of the C–N linkage, inferred from the bond lengths of 1.342(4) and 1.36(1) Å in the *cis* and *trans* compounds respectively. This contraction from the normal single-bond length of about 1.47 Å is unlikely to be related to the observed hydrogen bonding. The C=O bond lengths of 1.213(4) and 1.194(9) Å, respectively, appear to be normal.

The obvious mesomeric equilibrium (Robin *et al.*, 1971)



does not therefore provide an adequate description of the observed effects. It would be of interest to determine if screening of the C–N internuclear repulsion by the nitrogen lone pair (Boeyens, 1982) could better account for the shortening of the bond, as well as the increased barrier to rotation. This effect will be sensitive to both electronic and steric influences of neighboring substituents, on the nitrogen atom as well as the aryl ring.

It is of interest to note that in the known structures of *p*-substituted acetanilides (Brown, 1966; Haisa *et al*, 1974, 1976, 1977; Patel *et al* 1983; Subramanian, 1966; Andreetti *et al.*, 1968), there is a sympathetic relationship between the two N–C bonds, rather than the amide bonds implicated by Robin *et al.* (1971). The sum of the N–C bond lengths in each of these compounds is 2.765 Å. Mesomeric electron donor substituents in the *para* position have a clear effect on the *N*-aryl bond length, presumably by electrostatic repulsion of the nitrogen lone pair, which then causes more effective screening of the nuclei in the *N*-carbonyl bond region. For compounds with a *para* mesomeric donor, the *N*-aryl bond length exceeds 1.42 Å, but for neutral substituents it is less than 1.42 Å. An inverse relationship around 1.34 Å exists for the *N*-carbonyl bonds. More structural work is needed to substantiate these ideas in more detail.

The structure of **3** agrees with the previous observations. The *N*-carbonyl bond of 1.316(9) Å is, once again, unexpectedly short; the C–N–C=O fragment is virtually planar [ϕ = 2.9(9)°] with the amide group bent considerably out of the aromatic plane [ϕ = 163.2(9)°]. The C=O bond length is a normal 1.227(8) Å long.

The present results seem to confirm the proposal of Siddall *et al.* (1968) that for amides the *trans* configuration is favored over the *cis*, although our single result indicates that this could be reversed for thioamides.

Acknowledgment

We thank the Foundation for Research Development and the University of the Witwatersrand for comprehensive financial support.

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Structure factor data have been deposited with The British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60553 (20 pages).