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N-(1-Methyl-2-pyrrolidinylidene)-*p*-toluenesulfonamide: a Condensation Product of 4-Methylphenylsulfonyl Isocyanate and 1-Methyl-2-pyrrolidone

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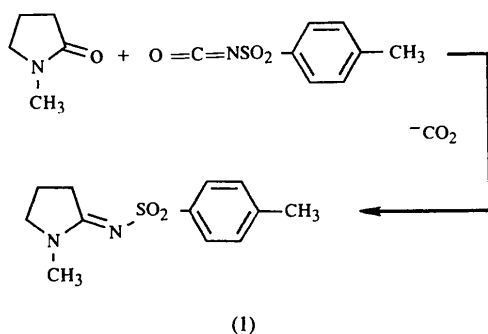
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Abstract

The preparation of the crystalline title compound, C₁₂H₁₆N₂O₂S, which is shown to have *E* geometry about the imine double bond, also yields an oily *Z* isomer.

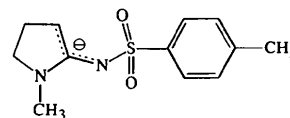
Comment

The reaction of highly polar 4-methylphenylsulfonyl isocyanate (*p*-tosyl isocyanate, TSI) with amides is well known (Logemann, Artini, Tosolini & Piccini, 1958; King, 1959). In particular, its reaction with 1-methyl-2-pyrrolidinone is exothermic and yields the title compound, *N*-(1-methyl-2-pyrrolidinylidene)-*p*-toluenesulfonamide, (1).



The early reports on the preparation of compound (1) do not describe its stereochemistry. A more recent publication (Magnus & Moursounidis, 1991) on the reactions of the anion of the iminopyrrolidine, (2), with carbonyl compounds infers an *E* geometry about the imine bond following X-ray diffraction studies on three of its condensation products with ketones. This deduction, however, presupposes that the intermediate anion (2), which has either a tautomeric or resonance-

stabilized structure, cannot rotate about the imino bond. In such circumstances, rotation is a strong possibility. For these reasons and because of work in progress with compound (1), it was decided to repeat the synthesis and to carry out a structural study.



(2)

In the absence of solvent, reaction of TSI with 1-methyl-2-pyrrolidinone afforded two isomeric products. One was the previously described crystalline compound (1), but the other, an oil, appears to be the opposite *Z* isomer. X-ray analysis showed compound (1) to be the *E* isomer shown in Fig. 1. As this present work demonstrates that the crystalline compound (1) used for the condensations discussed above (Magnus & Moursounidis, 1991) must have been the *E* isomer, we have shown that formation of the anion (2), by reaction of (1) with base, does not change the *E* geometry and therefore that the suppositions arising from previous X-ray structural studies on condensation products were correct.

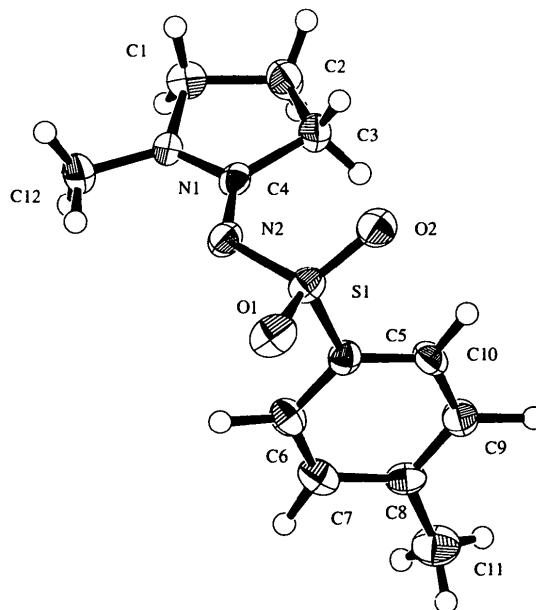


Fig. 1. A perspective view of the title compound showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been assigned arbitrary radii.

Experimental

Under moisture-free conditions, 1-methylpyrrolidine (2.45 ml, 25 mmol) was added gradually to fresh 4-methylphenyl-

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sulfonyl isocyanate (3.42 ml, 22.5 mmol), with the reaction flask temperature kept at about 313 K. Effervescence was observed and after about 15 min, a yellow solid began to separate. After 30 min at 313 K, the reaction mixture was quenched with water (25 ml) and extracted with dichloromethane. The organic solution was dried (Na₂SO₄) and evaporated to yield a yellow semi-solid residue (6.25 g) which was crystallized from petroleum ether (b.p. 313–333 K)/ethyl acetate (1:1 v/v). The crystals of the title compound (1) were recrystallized from ethyl acetate (m.p. 438–439 K). Found: C 57.3, H 6.4, N 11.1%; C₁₂H₁₆N₂O₂S requires C 57.1, H 6.4, N 11.1%. ¹H NMR (CDCl₃): δ 2.03 (2H, q, J = 7.8 Hz), 2.39 (3H, s), 2.96 (3H, s), 3.00 (2H, t, J = 7.8 Hz), 3.45 (2H, t, J = 7.8 Hz); MS (M⁺): m/z 252. From the mother liquors of the first crystallization, after chromatography on silica gel (elution with ethyl acetate/chloroform, 1:1), an oil was isolated as a single component, which on the basis of its NMR and mass spectra appeared to be the Z isomer of the title compound (it was not purified further); ¹H NMR (CDCl₃): δ 2.02 (2H, q, J = 7.7 Hz), 2.38 (2H, t, J = 7.7 Hz), 2.41 (3H, s), 2.84 (3H, s), 3.39 (2H, t, J = 7.7 Hz), 7.27 (2H, d, J = 8.2 Hz), 7.80 (2H, d, J = 8.2 Hz); MS (M⁺): m/z 252.

Crystal data

C₁₂H₁₆N₂O₂SM_r = 252.33

Monoclinic

P2₁/n

a = 8.469 (8) Å

b = 13.474 (8) Å

c = 11.256 (9) Å

β = 106.29 (6)°

V = 1232 (1) Å³

Z = 4

D_x = 1.359 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 13 reflections

θ = 3.53–5.99°

μ = 0.243 mm⁻¹

T = 153 K

Prism

0.30 × 0.20 × 0.20 mm

Colourless

Data collection

Rigaku AFC-6S diffractometer

ω/2θ scans

Absorption correction: none

2512 measured reflections

1993 independent reflections

1414 observed reflections

[I > 3σ(I)]

R_{int} = 0.052θ_{max} = 24.99°

h = 0 → 10

k = 0 → 16

l = -13 → 13

3 standard reflections

monitored every 150

reflections

intensity decay: 20%

(see text)

Refinement

Refinement on F²

R = 0.0549

wR = 0.0579

S = 1.977

1403 reflections

154 parameters

H atoms placed in calculated positions and not refined

w = 1/[σ²(F²) + 0.3F²]^{1/2}(Δ/σ)_{max} = 0.03Δρ_{max} = 0.28 e Å⁻³Δρ_{min} = -0.43 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables**for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	x	y	z	U _{eq}
S1	0.3241 (1)	0.16269 (8)	0.57524 (10)	0.0329
O1	0.3004 (4)	0.1437 (2)	0.6953 (3)	0.0451
O2	0.2094 (3)	0.1153 (2)	0.4702 (3)	0.0398
N1	0.7295 (4)	0.1254 (2)	0.5038 (3)	0.0286
N2	0.5135 (4)	0.1375 (3)	0.5888 (3)	0.0330
C1	0.7751 (5)	0.1178 (3)	0.3873 (4)	0.0344
C2	0.6157 (5)	0.1426 (3)	0.2887 (4)	0.0405
C3	0.4800 (5)	0.1369 (3)	0.3532 (4)	0.0341
C4	0.5700 (5)	0.1349 (3)	0.4909 (4)	0.0275
C5	0.3062 (5)	0.2924 (3)	0.5500 (4)	0.0289
C6	0.4123 (5)	0.3568 (3)	0.6334 (4)	0.0346
C7	0.3935 (5)	0.4582 (3)	0.6167 (4)	0.0382
C8	0.2698 (5)	0.4987 (3)	0.5176 (4)	0.0325
C9	0.1680 (5)	0.4336 (3)	0.4348 (4)	0.0360
C10	0.1857 (5)	0.3319 (3)	0.4508 (3)	0.0323
C11	0.2512 (6)	0.6090 (3)	0.5052 (5)	0.0474
C12	0.8537 (5)	0.1137 (3)	0.6213 (4)	0.0407

Table 2. Selected geometric parameters (Å, °)

S1—N2	1.604 (4)	N2—C4	1.319 (6)
S1—C5	1.771 (4)		
O1—S1—N2	105.7 (2)	S1—N2—C4	120.9 (3)
O2—S1—N2	114.1 (2)	N1—C4—N2	120.6 (3)
N2—S1—C5	105.2 (2)	N2—C4—C3	130.9 (4)
S1—N2—C4—N1	172.1 (3)	O2—S1—C5—C10	6.5 (5)
O1—N2—C4—C3	-10.7 (6)	N2—S1—C5—C6	-53.6 (4)
O1—S1—N2—C4	171.2 (3)	N2—S1—C5—C10	128.2 (4)
O2—S1—N2—C4	41.7 (4)	C4—N2—S1—C5	-75.5 (3)
O2—S1—C5—C6	-175.4 (4)		

The standard intensities decayed by 20% over the ca 35 h period of data collection and a decay correction was therefore applied as part of the data reduction process

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- King, C. (1959). *J. Org. Chem.* pp. 352–356.
 Logemann, W., Artini, D., Tosolini, G. & Piccini, F. (1958). *Chem. Ber.* pp. 951–956, 2566–2574.
 Magnus, P. & Moursounidis, J. (1991). *J. Org. Chem.* pp. 1529–1534.
 Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.