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NATURALLY-OCCURRING ACETYLENIC COMPOUNDS AND DERIVATIVES

REGIO- AND STEREOCONTROLLED CHLOROFORMYLATION OF 2-(1-PROPYNYL)THIOPHENE AND 2-PHENYL-5-(1-PROPYNYL)THIOPHENE

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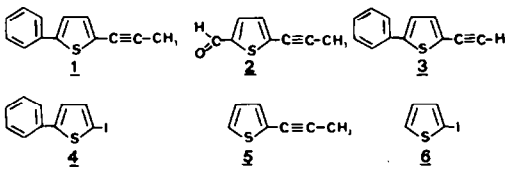
Abstract—2-Phenyl-5-(1-propynyl)thiophene (**1**), isolated from *Coreopsis grandiflora*, and 2-(1-propynyl)thiophene (**5**), an immediate precursor in the synthesis of junipal (**2**), were synthesized in high yield by a Pd-catalyzed reaction between propyne and 2-iodo-5-phenylthiophene (**4**) or 2-iodothiophene (**6**), respectively. Reaction of **5** with the Vilsmeier reagent derived from $POCl_3$ and N-methylformanilide (MFA) afforded a mixture from which it was possible to isolate (*E*)-3-chloro-2-methyl-3-(2-thienyl)acrolein (**10**) in 37.7% yield. The structure and stereochemistry of **10** was unequivocally established by X-ray diffraction of a single crystal of the 2,4-dinitrophenylhydrazone of **10**. GLC analysis showed that **10** was contaminated by *ca* 7% with an isomer to which, on the basis of ^{1}H-NMR and mass spectra, the structure of (*Z*)-3-chloro-2-methyl-3-(2-thienyl)acrolein (**11**) was attributed.

Contrary to what was expected from the literature, junipal (**2**) represented only a minor component in the reaction mixture obtained by the Vilsmeier reaction on **5**.

Reaction of **1** with $POCl_3$ and MFA afforded (44.6% yield) a (*E*)-3-chloro-2-methylacrolein to which the structure **15** was attributed. Compound **15** was also contaminated by *ca* 10% of an isomer **16**, which very probably corresponded to the (*Z*)-stereoisomer of **15**.

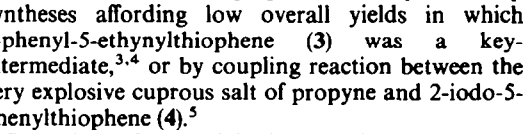
A common structural characteristic of several naturally-occurring thiophenes is the presence of a 1-propynyl group α-linked to a thiophene ring. Typical examples are 2-phenyl-5-(1-propynyl)thiophene (**1**), isolated from *Coreopsis grandiflora*,[1] and 2-(1-propynyl)-5-formylthiophene (junipal; **2**), an odoriferous constituent of the woodrotting fungus, *Daedalia juniperina*.[2]



Compound **1** has been prepared either by multi-step syntheses affording low overall yields in which 2-phenyl-5-ethynylthiophene (**3**) was a key-intermediate,[3,4] or by coupling reaction between the very explosive cuprous salt of propyne and 2-iodo-5-phenylthiophene (**4**).[5]

Several syntheses of junipal (**2**) have been also reported.[6-10] Two of them are based on 2,5-disubstituted thiophene ring forming reactions not suitable for the preparation of significant amounts of substance,[6,7] the other ones[8-10] involving the preparation of 2-(1-propynyl)thiophene (**5**) starting from 2-iodothiophene (**6**), followed by formylation. However, the overall yields were in any case rather low. It is also interesting to note that in two of these last reactions[8,9] the formylation was carried out by converting **5** into the corresponding 5-Li derivative, followed by reaction with DMF, in the last one[10] the formyl group was directly introduced by reacting **5** with phosphorus oxychloride and DMF.

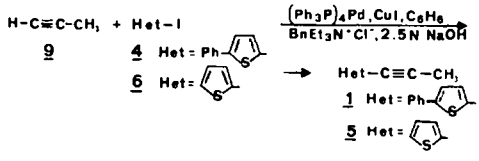
However, in our opinion the result of this last reaction appeared rather strange. In fact, apparently the electrophilic reaction occurred only on the thiophene ring, which had an electron-withdrawing 1-alkylnyl group in the α-position, and did not involve the C≡C triple bond of this group. On the other hand, the literature data show that either ethynylarenes (**7a**)[11,12] or 1-aryl-1-propynes (**7b**)[12] react with the Vilsmeier reagent derived from $POCl_3$ and DMF or MFA[13] (N-methylformanilide) to afford β-chloroacroleins (**8**) with undetermined stereochemistry.



In pursuing our work on the synthesis and reactivity of naturally-occurring acetylenic compounds and derivatives incorporating biologically active molecules,[14,15] it appeared interesting either to develop a simple and efficient synthesis of 2-(1-propynyl) thiophenes, or to reinvestigate the reaction of such compounds with Vilsmeier reagents.[16] We now

report a Pd-catalyzed synthesis of **1** and **5**, which can be used for the preparation of other functionally substituted 2-(1-propynyl)thiophenes, and the results obtained in the study of the reactions of **1** and **5** with the Vilsmeier reagent derived from $POCl_3$ and MFA.

Compounds **1** and **5** were prepared according to a previously reported general method for the synthesis of acetylenic heterocycles.[14] Thus 2-iodo-5-phenylthiophene (**4**) was reacted with a benzene solution of a molar excess of propyne (**9**), using a mixture of $(PPh_3)_4Pd$ (3.5 mole %) and CuI (5 mole %) as catalyst. The reaction was carried out at room temp for 7 hr, under a propyne atmosphere and phase-transfer conditions, employing benzyltriethylammonium chloride (3.5 mole %) as the phase-transfer agent and a large excess of 2.5 N NaOH as the base. Compound **1** was isolated into 80% yield by chromatography of a hexane solution of the crude reaction product (Scheme 1).



Scheme 1.

A similar Pd-catalyzed reaction was employed to prepare **5** in 93% yield starting from 2-iodothiophene (**6**) and **9**.

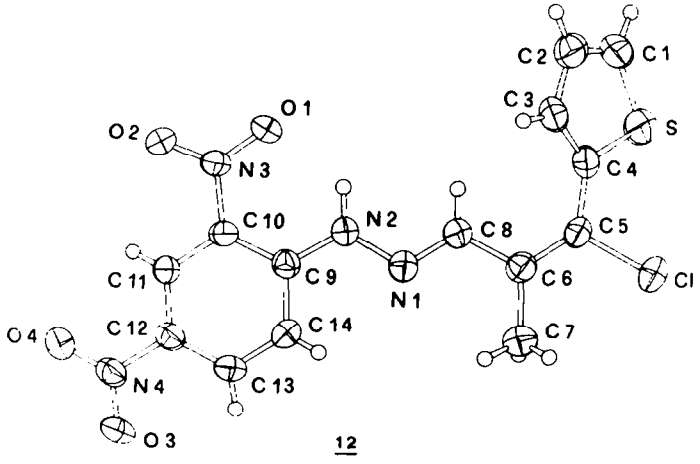
We attempted to convert **5** into junipal (**2**) with a Vilsmeier–Haack reaction.[10] Thus 0.5 equivalents of **3** were slowly added under stirring to an equimolar mixture of $POCl_3$ and MFA. After the exothermic reaction ceased, the mixture was heated at 60° for 1 hr, cooled at room temp and hydrolyzed. Analysis of the reaction products showed however that these consisted essentially of the starting materials. Therefore, the procedure was modified in the following way. An equimolar mixture of $POCl_3$ and MFA was stirred for 30 min. Then, 1 equivalent of **3** was slowly added to the orange mixture. After stirring for 4 hr at 30°, the mixture was maintained at room temp for 12 hr and hydrolyzed. GLC analysis of an ether solution of the crude mixture showed the presence of a main product together with four minor components. Purification by chromatography on a silica gel column resulted in the recovery of the main component (**10**) in a 37.7% yield from the first eluting fractions. GLC–MS analysis of **10** which had the molecular formula C_8H_7ClOS showed that it was contaminated by *ca* 7% with another compound (**11**). Examination of the mass spectra of **10** and **11** and of the ^{1}H-NMR spectrum of **10** contaminated by **11** established that **11** was a stereoisomer of **10**. On the other hand IR analysis showed that these compounds contained a formyl group, and ^{1}H-NMR analysis revealed that they contained also monosubstituted thiophene rings. Unfortunately, neither from the mass spectra nor from ^{1}H-NMR data registered in benzene or hexafluorobenzene solution, by application of the aromatic solvent induced shifts,[17] was it possible to determine unequivocally the structures of **10** and **11**.

The structure and stereochemistry of **10** was established by a single crystal X-ray analysis of the corresponding 2,4-dinitrophenylhydrazone (**12**). Details of the analysis are given in the Experimental section. A perspective view of **12** is given in Fig. 1. Bond lengths and bond angles, excluding hydrogen, are listed in Tables 1 and 2, respectively.

The resulting molecule lays in three planes. The first, which contained the atoms of the thienyl group, formed a dihedral angle of 133.6° with a second plane containing the C(4), C(5), Cl, C(6), C(7) and C(8) atoms. The last plane was almost coplanar (dihedral angle of 172.3°) with the plane containing the 2,4-$(NO_2)_2C_6H_3$—NH—N group (Fig. 1). A strong intramolecular hydrogen interaction was present between N(2) and O(1), the distance H(2N)–O(1) being 1.96(3)Å (Table 1).

Thus, on the basis of this X-ray analysis, the structures of (*E*)- and (*Z*)-3-chloro-2-methyl-3-(2-thienyl)acrolein were assigned to **10** and **11**, respectively.

Two other minor components were isolated (3.1% yield) from the final eluting fractions of the chromatography of the crude mixture. GLC–MS analysis showed that such compounds were in *ca* 1:1 ratio and were constituted of junipal (**2**) and a thiophene derivative, isomer of **10** and **11**, which presumably had structure **13**. In fact, the mass spectrum of **13**, which differed markedly from those of **10** and **11**, could be



12

Fig. 1. A perspective view of **12** with the atom numbering.

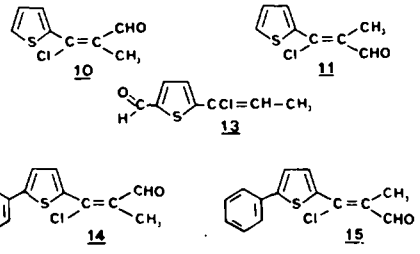
Table 1. Bond distances (Å) in **12** and their e.s.d.

S—C(1)	1.695(4)	N(2)—H(2N)	0.90(3)	N(3)—O(2)	1.218(3)
C(1)—C(2)	1.332(6)	C(6)—C(8)	1.460(4)	C(10)—C(11)	1.385(4)
C(2)—C(3)	1.412(6)	C(8)—N(1)	1.279(3)	C(11)—C(12)	1.363(4)
C(3)—C(4)	1.377(5)	N(1)—N(2)	1.383(3)	C(12)—N(4)	1.456(3)
C(4)—S	1.720(3)	N(2)—C(9)	1.357(3)	N(4)—O(3)	1.224(3)
C(4)—C(5)	1.457(4)	H(2N)—O(1)	1.96(3)	N(4)—O(4)	1.234(3)
C(5)—Cl	1.762(3)	C(9)—C(10)	1.413(4)	C(12)—C(13)	1.397(4)
C(5)—C(6)	1.340(4)	C(10)—N(3)	1.451(3)	C(13)—C(14)	1.351(4)
C(6)—C(7)	1.504(5)	N(3)—O(1)	1.240(3)	C(14)—C(9)	1.419(4)

interpreted on the basis of a structure containing a thiophene ring substituted with a formyl and a 1-chloro-1-propenyl group. Such a compound could be derived by addition of hydrogen chloride to junipal (**2**) during the hydrolysis of the very viscous reaction mixture obtained from **5**, $POCl_3$ and MFA.

Compound **1** was also reacted with the Vilsmeier reagent derived from $POCl_3$ and MFA. The reaction, which was carried out under experimental conditions similar to those employed for **5**, afforded a mixture of two compounds **14** and **15**, in a 44.6% yield. The mixture could not be separated into the single components by chromatography on a silica gel column. The ^{1}H-NMR spectrum of this mixture was similar to that of **10** and **11** and showed that **14** and **15** were very probably two stereoisomers in a *ca* 90:10 ratio.

On the basis of the analytic and spectroscopic data, and taking into account the results obtained in the reaction of **5** with $POCl_3$ and MFA, it was possible to assign to **14** and **15** the structures of (*E*)- and (*Z*)-3-chloro-2-methyl-3-(5-phenyl-2-thienyl)acrolein, respectively.



In conclusion, the results reported here show that the Pd-catalyzed reaction of 2-iodothiophenes with propyne represents a very simple and efficient method for the synthesis of 2-(1-propynyl)thiophenes. These compounds, react regioselectively with the Vilsmeier reagent derived from $POCl_3$ and MFA to afford 3-chloro-2-methyl-3-(2-thienyl)acroleins in satisfactory yields. Therefore, such alkylnylthiophenes behave in this reaction analogously to ethynylarenes[11,12] and 1-aryl-1-propynes.[12] Moreover, the results obtained indicate that, contrary to what was previously reported,[10] junipal (**2**) represents only a minor component of the complex reaction mixture derived from the reaction of **5** with $POCl_3$ and MFA.

X-ray diffraction data have also established that the chloroformylation reaction is rather (*E*)-stereoselective. On this subject, it must be noted that the stereochemical aspects of the chloroformylation reaction of alkynes had not been previously ascertained unequivocally.

Finally, it should be mentioned that these easily available 3-chloro-2-methyl-3-(2-thienyl)acroleins may represent useful synthons in pesticide chemistry.

Note added in proof: Biological tests carried out at the "Centro Ricerche Antiperassitari—FARMOPLANT (Milan) showed that compound **14** containing 10% of **15** showed high funeidal activity *in vitro* towards *Botrytis cinerea* and *Pythium irregulare*.

EXPERIMENTAL

^{1}H-NMR spectra were recorded at 60 MHz on a Varian T 60 spectrometer using TMS as internal standard. Mass spectra were recorded on a Hewlett–Packard 5995 A gas chromatograph/mass spectrometer. IR spectra were determined on a Perkin–Elmer 283 B spectrometer. GLC analyses were performed on a DANI 3900 glass capillary column dedicated gas chromatograph using a FFAP glass capillary column (25 m × 0.25 mm i.d.) and a FID detector. Liquid chromatographic purifications were carried out on a Jobin-Yvon "Chromatospac Prep" liquid chromatograph

Table 2. Angles (°) in **12** and their e.s.d.

C(4)—S—C(1)	91.6(2)	N(2)—H(2N)—O(1)	130(2)
S—C(1)—C(2)	113.2(5)	N(2)—C(9)—C(14)	119.9(2)
C(1)—C(2)—C(3)	112.3(3)	C(14)—C(9)—C(10)	116.1(2)
C(2)—C(3)—C(4)	112.6(3)	C(9)—C(10)—N(3)	122.8(2)
C(3)—C(4)—S	110.2(2)	C(9)—C(10)—C(11)	121.4(2)
C(3)—C(4)—C(5)	129.6(3)	C(10)—N(3)—O(1)	118.2(2)
S—C(4)—C(5)	120.1(2)	C(10)—N(3)—O(2)	119.4(2)
C(4)—C(5)—Cl	112.9(2)	O(1)—N(3)—O(2)	122.4(2)
C(4)—C(5)—C(6)	128.4(2)	C(10)—C(11)—C(12)	119.8(2)
Cl—C(5)—C(6)	118.6(2)	C(11)—C(12)—N(4)	119.3(2)
C(5)—C(6)—C(8)	119.7(2)	C(12)—N(4)—O(4)	117.7(2)
C(5)—C(6)—C(7)	112.8(2)	C(13)—C(12)—N(4)	120.1(2)
C(7)—C(6)—C(8)	117.4(2)	C(12)—N(4)—O(4)	117.7(2)
C(6)—C(8)—N(1)	119.5(2)	O(3)—N(4)—O(4)	123.3(2)
C(8)—N(1)—N(2)	115.8(2)	C(11)—C(12)—C(13)	120.5(2)
N(1)—N(2)—C(9)	118.8(2)	C(12)—C(13)—C(14)	119.9(3)
N(2)—C(9)—C(10)	123.9(2)	C(13)—C(14)—C(9)	122.0(3)
		C(14)—C(9)—C(10)	116.2(2)

using a Knauer differential refractometer as detector. TLC analyses were performed using Merck plastic sheets silica gel 60 F_{254}.

All reactions of air- and water-sensitive materials were performed in flame-dried glassware under nitrogen.

Tetrakis(triphenylphosphine)palladium was prepared according to the literature.

2-Phenyl-5-(1-propynyl)thiophene (**1**)

Typical procedure. A de-aerated soln of **4** (7 g, 24.5 mmol) in benzene (40 ml) was added to a mixture of benzyltriethylammonium chloride (0.18 g, 0.86 mmol), cuprous iodide (0.25 g, 1.22 mmol) and $(PPh_3)_4Pd$ (0.994 g, 0.86 mmol). The mixture was saturated at 5° with **9**. De-aerated 2.5 N aq NaOH (44 ml) was then added and the mixture was stirred under a propyne atmosphere at room temp. Monitoring by TLC showed that **4** had completely reacted after 7 hr. Sat NH_4Cl was then added and the resulting mixture, after stirring for 0.5 hr, was extracted with hexane and concentrated. The residue was purified by chromatography on a Merck H 60 silica gel column using hexane as eluant to afford **4** (3.88 g) in 80% yield: m.p. 44–45° (lit. m.p. 43–44°): ν_{max} (film): 3080, 3060, 3020, 2960, 2920, 2840, 2220, 1950, 1870, 1790, 1720, 1600, 1490, 1450, 1440, 1370, 1260, 1190, 1070, 1050, 1025, 955, 900, 800, 750, 680 and 640 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.96 (3H, s), 6.80–7.60 ppm (m, 7H). Mass spectrum: *m/e* 200 (4.9, M + 2), 199 (15.2, M + 1), 198 (100, M), 197 (45.7, M − 1), 171 (11.2), 165 (40.2), 164 (5.3), 160 (5.0), 153 (8.6), 152 (13.8), 151 (3.9), 139 (7.3), 127 (4.8), 87 (6.2), 86 (6.8), 85 (4.6), 83 (6.1), 82 (5.5), 77 (24.3), 76 (9.7), 75 (9.2), 74 (10.4), 69 (17.8), 63 (22.3), 62 (9.6), 52 (5.5).

2-(1-Propynl)thiophene (**5**)

This was prepared in 93% yield starting from **6** and **9** according to the procedure followed to synthesize **1**: b.p. 81°/15 torr (65–66°/7 torr)[8]; ν_{max} (film): 3100, 3080, 2950, 2915, 2840, 2220, 1515, 1425, 1370, 1240, 1190, 1075, 1040, 915, 840, 820 and 690 cm^{-1}. ^{1}H-NMR (CCl_4): δ 2.03 (3H, s), 6.70–7.17 ppm (m, 3H).

Reaction of **5** *with* $POCl_3$ *and MFA*

Pure $POCl_3$ (8.66 g, 56.5 mmol) was added to N-methylformanilide (7.64 g, 56.5 mmol). The mixture, stirred for 30 min, became orange coloured. Then **5** (6.9 g, 56.5 mmol) was slowly added. After stirring for 4 hr at 30°, the mixture was maintained at room temp for 12 hr without stirring. A saturated aqueous solution of AcONa was then added to the dark and viscous mixture which was stirred for 1 hr and extracted with ether. The ether soln was washed with 2 N HCl aq, $NaHCO_3$, water, dried over Na_2SO_4 and concentrated. The residue was analyzed by GLC on a FFAP glass capillary column and showed the presence of a main product **10**, together with four minor components. Purification by chromatography on a Merck H-60 silica gel column (185 g) using a 1 : 1 mixture of hexane and benzene as eluant, resulted in the recovery from the first eluting fractions of the main component **10** (4.29 g) in a 37.7% yield. (Found: C, 51.67; H, 4.12; Cl, 19.3. Calc for C_8H_7ClOS: C, 51.48; H, 3.79; Cl, 18.99); ν_{max} (film): 3100, 3080, 2960, 2920, 2860, 2750, 1670, 1590, 1510, 1420, 1390, 1370, 1350, 1250, 1225, 1180, 1075, 1045, 1010, 875, 825, 810 and 700 cm^{-1}. ^{1}H-NMR (CCl_4): δ 2.03 (s, 3H, CH_3; 93.5% by integration), 2.09 (s, 3H; CH_3; 6.5% by integration) 6.86–7.26 (m, 2H), 7.39–7.63 (m, 1H), 9.59 (s, 1H; CHO; 96.5% by integration), 10.30 ppm (s, 1H; CHO; 6.5% by integration).

GLC analysis on a FFAP or SE 54 glass capillary column showed that compound (**10**) was contaminated by *ca* 7% of a probable stereoisomer (**11**). GLC–MS analysis showed the mass spectra of **10** and **11** to be very similar. Compound **10** had the following mass spectrum: *m/e* 187 (M + 2, 2.5), 187 (M + 1, 1.5), 186 (M, 6.3), 185 (2.6), 151 (M—Cl, 100), 123 (53.9), 122 (21.3), 121 (36.4), 96 (6.2), 84 (10.8), 79 (19.0), 77 (18.8), 69 (10.1), 63 (12.7), 51 (16.3), 45 (65.2). Compound **11** had the following mass spectrum: *m/e* 186 (M, 8.1), 151 (M − Cl, 100), 123 (48.0), 122 (23.7), 121 (34.2), 96 (5.7), 84 (9.5), 79 (15.2), 77 (15.6), 69 (8.7), 63 (9.3), 51 (11.8), 45 (46.3).

Compound **10** was converted into the corresponding 2,4-dinitrophenylhydrazone (**12**) by reaction with a soln of 2,4-dinitrophenylhydrazine in EtOH containing H_2SO_4. Compound **12** (recrystallised from acetone) had a m.p. 133–135°. (Found: N, 15.1%. Calc for $C_{14}H_{11}ClN_4O_4S$: N, 15.3%.)

Two other minor components (**2** and **13**), of the crude mixture were isolated (3.1% yield) from the final eluting fractions of the chromatography. Compound **2** had the following mass spectrum: *m/e* 152 (M + 2, 5.0), 151 (M + 1, 11), 150 (M, 100), 149 (M − 1, 53.2), 121 (46.3), 93 (3.7), 78 (5.0), 77 (26.5), 69 (10.0), 63 (9.2), 62 (5.7), 61 (4.8), 51 (16.8), 45 (12.7). This spectrum was very similar to that of an authentic sample of junipal (**2**) prepared from **5**. Compound **13** had the following mass spectrum: *m/e* 188 (M + 2, 7.9), 187 (M + 1, 2.5), 186 (M, 21.1), 151 (8.2), 123 (2.3), 111 (100), 84 (1.6), 83 (8.1), 82 (2.7), 75 (3.3), 57 (5.7), 44 (6.4).

Reaction of **1** *with* $POCl_3$ *and MFA*

Following the procedure described above, **1** (2 g, 10.1 mmol) was reacted with a mixture of $POCl_3$ (1.55 g, 10.1 mmol) and MFA (1.37 g, 10.1 mmol). After 4 hr at 35° and 12 hr at room temp the mixture was hydrolyzed with a sat soln of AcONa and extracted with benzene.

The benzene extracts were washed with 2 N HCl, aq $NaHCO_3$, water, dried over Na_2SO_4 and concentrated *in vacuo* to afford a residue (1.49 g). This was purified by chromatography on a silica gel column (185 g) using benzene as eluant, to afford **14** (1.23 g, 46.4% yield): m.p. 87–89°. (Found: C, 64.36; H, 4.27; Cl, 13.6. Calc for $C_{14}H_{11}ClOS$: C, 63.99; H, 4.2; Cl, 13.49%.) TLC analysis showed that **14** was contaminated by an impurity (**15**). The percentage of the impurity (*ca* 10%) was evaluated by examination of the ^{1}H-NMR spectrum of **14** in $CDCl_3$: δ 2.12 (s, 3H; CH_3; *ca* 90% by integration), 2.22 (s, 3H; CH_3; *ca* 10% by integration), 6.95–7.64 (m, 7H), 9.69 (s, 1H; CHO; *ca* 90% by integration), 10.27 ppm (s, 1H, CHO; *ca* 10% by integration). ν_{max} (KBr): 3080, 2860, 1720, 1575, 1440, 1385, 1340, 1265, 1230, 1150, 1070, 1005, 950, 910, 880, 840, 820, 745 and 690 cm^{-1}. MS: *m/e* 264 (M + 2, 12.5), 263 (M + 1, 6.2), 262 (M, 33.3), 232 (3.7), 229 (6.2), 228 (16.1), 227 (100), 199 (38.5), 198 (15.6), 197 (20.8), 184 (19.8), 165 (21.9), 160 (17.7), 121 (18.7), 115 (12.0), 77 (9.9), 69 (5.7), 63 (6.3), 51 (7.5).

X-ray analysis of **12**

Suitable crystals for X-ray investigation were obtained by slow evaporation of an acetone soln of the 2,4-dinitrophenylhydrazone of **10**. The crystal of **12** selected had dimensions of $1.20 \times 0.35 \times 0.25$ mm^3. Unit cell dimensions and space group symmetry were obtained by Weissenberg photographs. Accurate cell constants were obtained by a least-squares refinement using 25 selected high angle reflections collected by means of a Nicolet R 3 single crystal diffractometer with graphite-monochromatized Mo–Kα radiation. The same instrument was used for intensity data collection, using an ω scanning technique, and measuring the reflections $\pm h$, $+K$, $+l$, to a maximum θ angle of 22.5. Crystal data: $C_{14}H_{11}ClN_4O_4S$, M.W. 366.8, monoclinic, space group $P2_{1/c}$, a = 12.352(3), b = 11.287(3), c = 11.214(3) Å, β = 93.56 (2), v = 1560.4 Å^3, Z = 4, α_c = 1.561 g cm^{-3}, λ = 0.71069 (Mo–Kα), μ (Mo–Kα) 4.06 cm^{-1}; 2728 independent reflections were collected and 2316 with Fo > 4 σ (Fo) were used in the calculations. The intensity data were corrected for Lorentz and polarization factors, but not for absorption owing to the low absorption coefficient. The structure was easily resolved by direct methods and refined with isotropic thermal parameters to an R factor of 0.16. The introduction of anisotropic thermal parameters for all the heavy atoms reduced the R factor to 0.07 and the difference Fourier map showed the position of all the H-atoms.

They were introduced in the calculations with isotropic thermal factors equal to those of the bonded heavy atoms. A weighting scheme was also applied to Fo using $W = 1/(\sigma^2 Fo$

Table 3. Final fractional coordinates for heavy atoms and their e.s.d.

	Ueq = 1/3 ($U_{11}+U_{22}+U_{33}+2U_{13}$ cos)		
	X/A	Y/B	Z/C
Cl	0.55859(6)	0.23167(7)	0.61125(9)
S	0.35271(7)	0.07081(7)	0.51868(9)
O(1)	−0.0084(2)	0.6110(2)	0.4297(2)
O(2)	−0.1126(2)	0.7630(2)	0.4412(2)
O(3)	−0.0332(2)	1.0806(2)	0.7035(2)
O(4)	0.1161(2)	1.0824(2)	0.8151(2)
N(1)	0.2872(2)	0.5693(2)	0.5792(2)
N(2)	0.1856(2)	0.6074(2)	0.5417(2)
N(3)	−0.0281(2)	0.7111(2)	0.4682(2)
N(4)	0.0555(2)	1.0389(2)	0.7352(2)
C(1)	0.2687(3)	0.0453(3)	0.3961(3)
C(2)	0.2547(3)	0.1401(3)	0.3260(3)
C(3)	0.3147(3)	0.2388(3)	0.3702(3)
C(4)	0.3707(2)	0.2160(2)	0.4778(3)
C(5)	0.4354(2)	0.2955(2)	0.5558(2)
C(6)	0.4115(2)	0.4056(2)	0.5902(2)
C(7)	0.4864(3)	0.4781(3)	0.6722(3)
C(8)	0.3067(2)	0.4576(2)	0.5521(2)
C(9)	0.1542(2)	0.7149(2)	0.5811(2)
C(10)	0.0520(2)	0.7665(2)	0.5503(2)
C(11)	0.0218(2)	0.8735(2)	0.5986(2)
C(12)	0.0911(2)	0.9307(2)	0.6785(2)
C(13)	0.1943(2)	0.8850(3)	0.7081(3)
C(14)	0.2249(3)	0.7814(3)	0.6600(3)

+0.0009 Fo^2). The final least-squares cycle dropped the R factor to 0.051 and R_w to 0.059.

Atomic scattering factors for neutral atoms were taken from Cramer and Mann[18] and that of H-atoms from Stewart *et al.*[19] Final atomic coordinates are shown in Table 3. A perspective view of the molecule drawn using an ORTEP program[20] is given in Fig. 1. All calculations were made using the programs contained in SHELX[21] and X-RAY systems.[22]

Supplementary material

Lists of observed and calculated structure factors, final anisotropic parameters for heavy atoms, positional and thermal parameters for hydrogen atoms have been deposited at the Cambridge Crystallographic Data Center.

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