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The condensation of *p*-nitrothiophenol with formaldehyde and trichloroacetaldehyde. Structure of 2,2-bis(4′-nitro-1′-mercaptophenyl)-1,1,1-trichloroethane

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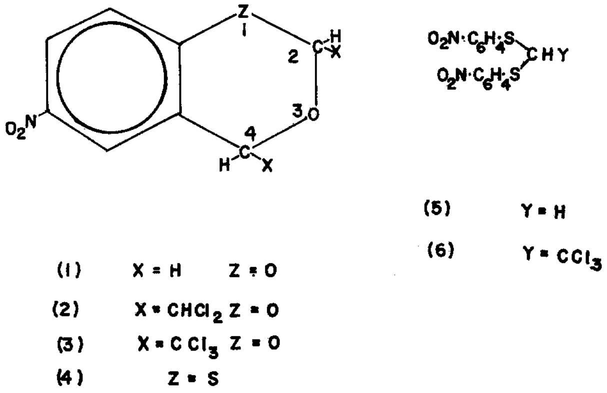
The condensation of *p*-nitrothiophenol with formaldehyde and with trichloroacetaldehyde is described. 2,2-Bis(4′-nitro-1′-mercaptophenyl)-1,1,1-trichloroethane is monoclinic, $P2_1/c$, a = 7.717(2), b = 34.666(5), c = 7.258(1) (Å), β = 116.32 (1) (deg.), V = 1740.35 (Å^3), Z = 4. The structure was solved by direct methods, from data collected at room temperature on an Enraf-Nonius CAD4 diffractometer, and refined by full-matrix least squares to a final R value of 0.052 using 1722 reflections. The torsion angles S—C—S—C_{Ar} are 159.7(3) and −90.5(4) (deg). The mean planes of the aromatic rings are at 46.8(2) (deg.) to one another. Evidence of intramolecular crowding is given by the inequality of several pairs of angles which would otherwise have been expected to be equal. The bond lengths are normal.

Introduction

4-Nitrophenol condenses readily with formaldehyde to give 6-nitro-1,3-benzodioxin (**1**) (Borsche and Berkhout, 1904; Chattaway and Goepp, 1933) and with dichloroacetaldehyde and trichloroacetaldehyde to give 6-nitro-2,4-bis(dichloromethyl or trichloromethyl)-1,3-benzodioxins, respectively (**2**) (Chattaway and Morris, 1928) (**3**) (Chattaway 1926). The X-ray crystal structure of these compounds has been reported. (Irving *et al.*, 1986–1988).

It was hoped that similar condensations with 4-nitrothiophenol would lead to corresponding members of the 1,3-benzothioxan heterocycle (e.g., **4**; 2 = S) for this system is represented by only a few members viz. 2-methyl-4-keto-1,3-benzothioxan (Mowry *et al.*, 1947) and 2-D-galactopentaacetoxypropyl-3,1-oxathian-4-one (Somogyi, 1987).



Scheme 1. Condensation products of *p*-nitrophenol and *p*-nitrothiophenol.

In the event the condensation of 4-nitrothiophenol and formaldehyde gave 1,1-bis(4′-nitro-1′-mercaptophenyl) methane (**5**), and the condensation of chloral with 4-nitrothiophenol gave 2,2-bis(4′ nitro-1′ mercaptophenyl)-1,1,1-trichloroethane (**6**) in good yield. That the aldehydes had not condensed to form analogs of diphenylmethane or DDT (Haskelberg and Lavie, 1947, 1949) was established by proton NMR spectroscopy and confirmed by the X-ray crystallographic structure determination of compound (**6**).

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Experimental

Preparation of bis(1′-mercapto-4′-nitrophenyl)methane (5)

Water (5 cm^3) and concentrated sulphuric acid (15 cm^3) were mixed, cooled to 10°C and added in one portion to 4-nitrothiophenol (2.0 g) dissolved in 40% Formalin and after 30 min the solution was diluted with water and a precipitate collected; washed well with water, dilute ammonia solution, and again with water. After the product had been air-dried it was recrystallized from boiling ethanol (very sparingly soluble) and glacial acetic acid (moderately soluble) as golden yellow platelets mp. 166–169°C without decomposition. Found: C, 48.95; H, 2.8; N, 8.8%. $C_{13}H_{10}N_2O_4S_2$ requires C, 48.63; H, 3.12; N, 8.69%.

Preparation of 2.2-bis(1′-mercapto-4′-nitrophenyl)-1,1,1-trichloroethane (6)

4-Nitrothiophenol (9.2 g; 1 mol) was added in small portions to a vigorously stirred solution of chloral hydrate (40 g; 2.4 mol.) in concentrated sulfuric acid (50 cm^3). A curdy precipitate appeared in the deep red solution after 30 min and after 48 hr the whole was poured over crushed ice. The precipitate was collected (sintered glass), washed well with water, dried, and crystallized to constant melting point from benzene from which the title compound (**6**) separated as well-formed, pale yellow platelets, mp. 115–117°C. Found: C, 38.4; H, 2.2; N, 6.4% $C_{14}H_9N_2O_4S_2Cl_3$ requires C 38.24; H, 2.06; N, 6.37%. The NMR spectrum (90 MHz in $CDCl_3$ gave δ (^1H) = 5.30[1H, *s* 2C*H*]; 7.59[4H, *d*, *t*, 4H(3)]; 8.11 [4H, *d*, *t*, 4H(2)]; $J_{2,3}$ = 9; $J_{2,6}$ = $J_{2,5}$ = 1 Hz. When the condensation was attempted with a large excess (> 8 mol) of chloral hydrate only a small amount of an unidentified product, very sparingly soluble in all common solvents, was isolated from the very viscous reaction product. The compound (**6**) did not react with methyliodide or 1,3 dibromo- or diiodo-methane to give a 5-ring even after being heated under reflux with benzene for 12 hr. It did not form a metal complex with Cu^{2+}, Ni^{2+}, or $(CH_3)_2Sn^{2+}$ ions.

Crystal data

Monoclinic, $P2_1/c$ (No. 14), a = 7.717(2), b = 34.666(5), c = 7.258(1) (Å), β = 116.32(1) (deg), V = 1740.35 $Å^3$, Z = 4, M_r for $C_{13}H_9O_4Cl_3N_2S_2$ = 427.70, D_c = 1.63 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 7.78 cm^{-1}, F(000) = 864, room temperature.

Data collection

Specimens with dimensions 0.06 × 0.16 × 0.34 mm were used for X-ray work. Lattice parameters determined by least-squares fitting of the setting angles of 24 reflections 16° < θ < 17°, automatically centered on a CAD4 diffractometer. Intensities were collected with graphite monochromated Mo $K\alpha$ radiation, λ = 0.71069 Å. $\omega/2\theta$ scan mode, variable scan rate, scan width (0.80 + 0.35tan θ) deg in ω, aperture width (1.12 + 1.05 tan θ) mm, range of reflections 1-25° in θ, 3371 reflections measured, 2468 unique, R_{int} = 0.040, 1722 [F_0 > $4\sigma(F_0)$] used in refinement, index range h 8/-8, k 41/0, 1 9/0. Three intensity control reflections (−2 7 6, 1 1

Table 1. Fractional atomic coordinates (×10^4) and Thermal Parameters (Å × 10^3) with esd's in parentheses for the title compound

Atom	*x/a*	*y/b*	*z/c*	U_{iso}/U_{eq}^a
C(1)	−72(8)	6327(2)	5166(9)	40(3)^a
H(1)	−1201(8)	6409(2)	3970(9)	38(17)
C(2)	1355(9)	6177(2)	4394(9)	43(3)^a
Cl(1)	366(3)	5779(1)	2750(3)	60(1)^a
Cl(2)	1808(2)	6542(1)	2922(3)	59(1)^a
Cl(3)	3587(2)	6048(1)	6450(3)	59(1)^a
S(11)	1112(2)	6711(1)	7021(3)	56(1)^a
C(11)	−820(8)	7028(2)	6671(9)	42(3)^a
C(12)	−400(9)	7421(2)	6735(8)	41(3)^a
H(12)	842(9)	7504(2)	6887(8)	54(19)
C(13)	−1755(8)	7686(2)	6587(9)	42(3)^a
H(13)	−1463(8)	7956(2)	6668(9)	76(24)
C(14)	−3529(8)	7565(2)	6324(9)	38(3)^a
C(15)	−3982(9)	7179(2)	6268(9)	49(3)^a
H(15)	−5231(9)	7100(2)	6117(9)	59(20)
C(16)	−2621(9)	6910(2)	6423(10)	53(4)^a
H(16)	−2917(9)	6639(2)	6366(10)	86(26)
N(11)	−4978(8)	7853(2)	6225(8)	49(3)^a
O(11)	−4534(7)	8193(1)	6272(8)	71(3)^a
O(12)	−6530(7)	7741(1)	6053(8)	68(3)^a
S(21)	−766(2)	5966(1)	6536(3)	49(1)^a
C(21)	−2615(8)	5689(2)	4596(9)	39(3)^a
C(22)	−2475(9)	5292(2)	4834(9)	45(3)^a
H(22)	−1351(9)	5179(2)	5923(9)	45(17)
C(23)	−3935(8)	5061(2)	3515(9)	45(3)^a
H(23)	−3835(8)	4786(2)	3675(9)	37(16)
C(24)	−5534(8)	5222(2)	1974(9)	39(3)^a
C(25)	−5692(9)	5616(2)	1641(9)	48(3)^a
H(25)	−6795(9)	5727(2)	519(9)	40(17)
C(26)	−4203(9)	5845(2)	2982(10)	48(4)^a
H(26)	−4278(9)	6120(2)	2788(10)	91(27)
N(21)	−7120(8)	4970(2)	615(8)	52(3)^a
O(21)	−6985(7)	4628(2)	971(8)	72(3)^a
O(22)	−8484(7)	5121(2)	−771(7)	84(3)^a

[a] Equivalent isotropic U calculated from anisotropic U: $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^+ a_j^+ a_i \cdot a_j$.

5, −3 22 3) monitored after every hour of data collection, showed an average decline in intensity of 1.4%. Data were corrected for background, scan speed, Lorentz and polarization factors; empirical absorption correction was applied (North *et al.*, 1968), with transmission factors 0.919 to 0.970.

Structure solution and refinement

Structure was solved by direct methods. Least squares anisotropic refinement (based on F) of positions of non-hydrogen atoms. Hydrogen atoms were constrained to idealized positions and assigned isotropic thermal parameters. Final $R = 0.052$, $wR = 0.045$, $w = 1/\sigma^2(F_0)$, $S = 5.36$, $\Delta/\sigma < 0.001$, residual electron density $-0.37 < \Delta\rho < +0.38$ e Å^{-3}. Complex neutral-atom scattering factors were from Stewart *et al.*, for hydrogen (1965) and from Cromer and Mann (1968) for all other atom types; dispersion corrections were from Cromer and Liberman (1970). Final atomic parameters are listed in Table 1. Computer programmes used SHELX76 (Sheldrick, 1978); SHELX86 (Sheldrick, 1985); PLUTO (Galloy *et al.*, 1989); PARST, Nardelli, 1983). All calculations were performed at the Computer Centre of the University of Cape Town on a VAX8550 computer.

Discussion

A view of the molecule is given in Fig. 1. Selected molecular parameters are reported in Table 2. The conformation of the molecule is such that the two S—C_{Ar} bonds are on the same side of the plane containing the atoms S(11), C(1), S(21). The orientations of the two S—C_{Ar} bonds with respect to this plane are different: S(11)—C(11) is perpendicular to it while S(21)—C(21) is approximately coplanar (see torsion angles in Table 1). The angle between the mean planes of the carbon atoms in the aromatic rings is 46.8(2) (deg). Evidence of crowding in the molecule is given by some short intramolecular distances: (Cl(1) · · · S(21), 3.296(4) and Cl(2) · · · S(11), 3.301(3); H(1) · · · H(26), 2.369(9) and H(16) · · · S(21), 2.837(7); Cl(1) · · · C(21), 3.150(8)(Å)); by the inequality of the two pairs of the angles S—C_{Ar}—C_{Ar} and by the inequality of the two S—C—C(Cl_3) angles (see Fig. 1 and Table 2). The bond lengths and angles are normal although certain pairs of angles which might have been expected to be equal (v.s.) are affected by steric crowding. The results of only a few X-ray structure determinations of compounds containing the $C(S-C_6H_4X)_2$ group have been reported viz. bis(4-bromophenylthio)methane (**7**) (Berthou *et al.*, 1970), hexakis(phenylthio)ethane (**8**) (Roelofsen *et al.*, 1974) and D-ribose-diphenyl-dithioacetal (**9**) (Ducruix

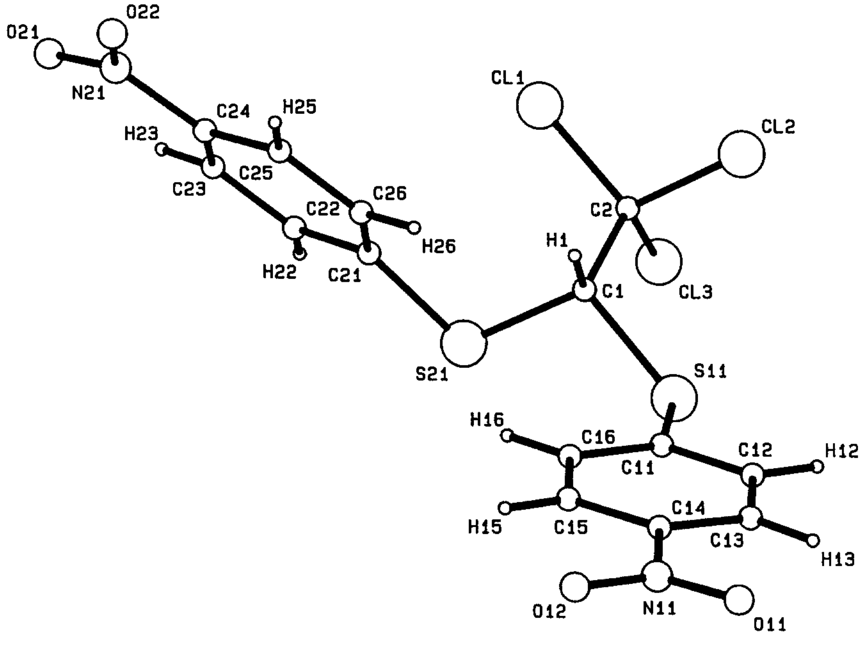

Fig. 1. A perspective view of a molecule of the title compound showing the numbering scheme used.

Table 2. Selected bond lengths (Å), bond angles (deg.), and torsion angles (deg.), with esd's in parentheses, for the title compound

C(1)—C(2)	1.531(11)	S(11)—C(1)—S(21)	105.7(3)
C(1)—S(11)	1.825(7)	C(2)—C(1)—S(21)	113.6(5)
C(1)—S(21)	1.820(8)	C(2)—C(1)—S(11)	108.2(5)
C(2)—Cl(1)	1.761(7)	C(1)—C(2)—Cl(3)	111.6(5)
C(2)—Cl(2)	1.787(8)	C(1)—C(2)—Cl(2)	109.9(5)
C(2)—Cl(3)	1.765(6)	C(1)—C(2)—Cl(1)	110.4(5)
S(11)—C(11)	1.778(7)	Cl(2)—C(2)—Cl(3)	108.0(4)
C(11)—C(12)	1.397(10)	Cl(1)—C(2)—Cl(3)	110.0(4)
C(11)—C(16)	1.381(10)	Cl(1)—C(2)—Cl(2)	106.9(3)
C(12)—C(13)	1.360(10)	C(1)—S(11)—C(11)	103.4(3)
C(13)—C(14)	1.362(9)	S(11)—C(11)—C(16)	124.6(5)
C(14)—C(15)	1.379(10)	S(11)—C(11)—C(12)	115.5(5)
C(14)—N(11)	1.479(10)	C(12)—C(11)—C(16)	119.9(7)
C(15)—C(16)	1.371(10)	C(11)—C(12)—C(13)	119.8(7)
N(11)—O(11)	1.220(8)	C(12)—C(13)—C(14)	119.5(7)
N(11)—O(12)	1.213(9)	C(12)—C(13)—H(13)	120.2(8)
S(21)—C(21)	1.778(6)	C(13)—C(14)—N(11)	119.3(6)
C(21)—C(22)	1.385(10)	C(13)—C(14)—C(15)	121.9(7)
C(21)—C(26)	1.377(8)	C(15)—C(14)—N(11)	118.7(6)
C(22)—C(23)	1.368(8)	C(14)—C(15)—C(16)	118.9(7)
C(23)—C(24)	1.364(7)	C(11)—C(16)—C(15)	119.9(7)
C(24)—C(25)	1.383(10)	C(14)—N(11)—O(12)	118.5(6)
C(24)—N(21)	1.471(8)	C(14)—N(11)—O(11)	117.0(6)
C(25)—C(26)	1.383(8)	O(11)—N(11)—O(12)	124.5(7)
N(21)—O(21)	1.208(10)	C(1)—S(21)—C(21)	105.4(3)
N(21)—O(22)	1.206(7)	S(21)—C(21)—C(26)	124.0(5)
		S(21)—C(21)—C(22)	116.5(5)
		C(22)—C(21)—C(26)	119.3(6)
		C(21)—C(22)—C(23)	120.0(6)
		C(22)—C(23)—C(24)	120.0(6)
		C(23)—C(24)—N(21)	119.2(6)
		C(23)—C(24)—C(25)	121.7(6)
		C(25)—C(24)—N(21)	119.1(6)
		C(24)—C(25)—C(26)	117.7(6)
		C(21)—C(26)—C(25)	121.3(6)
		C(24)—N(21)—O(22)	117.4(7)
		C(24)—N(21)—O(21)	118.2(6)
		O(21)—N(21)—O(22)	124.4(7)
S(11)—C(1)—S(21)—C(21)		159.7(3)	
C(2)—C(1)—S(21)—C(21)		−81.9(5)	
C(2)—C(1)—S(11)—C(11)		147.5(5)	
S(11)—C(1)—C(2)—Cl(3)		52.7(6)	
S(11)—C(1)—C(2)—Cl(2)		−67.0(5)	
S(11)—C(1)—C(2)—Cl(1)		175.3(4)	
S(21)—C(1)—C(2)—Cl(3)		−64.3(6)	
S(21)—C(1)—C(2)—Cl(2)		176.0(3)	
S(21)—C(1)—C(2)—Cl(1)		58.3(6)	
S(21)—C(1)—S(11)—C(11)		−90.5(4)	
C(1)—S(11)—C(11)—C(12)		−139.7(5)	
C(1)—S(11)—C(11)—C(16)		42.7(7)	
C(13)—C(14)—N(11)—O(11)		4.0(9)	
C(13)—C(14)—N(11)—O(12)		−177.8(6)	
C(15)—C(14)—N(11)—O(11)		−179.8(6)	
C(15)—C(14)—N(11)—O(12)		−1.6(9)	
C(1)—S(21)—C(21)—C(22)		134.7(5)	
C(1)—S(21)—C(21)—C(26)		−49.5(7)	
C(23)—C(24)—N(21)—O(21)		3.2(10)	
C(23)—C(24)—N(21)—O(22)		−177.7(6)	
C(25)—C(24)—N(21)—O(21)		−177.6(7)	
C(25)—C(24)—N(21)—O(22)		1.5(10)	

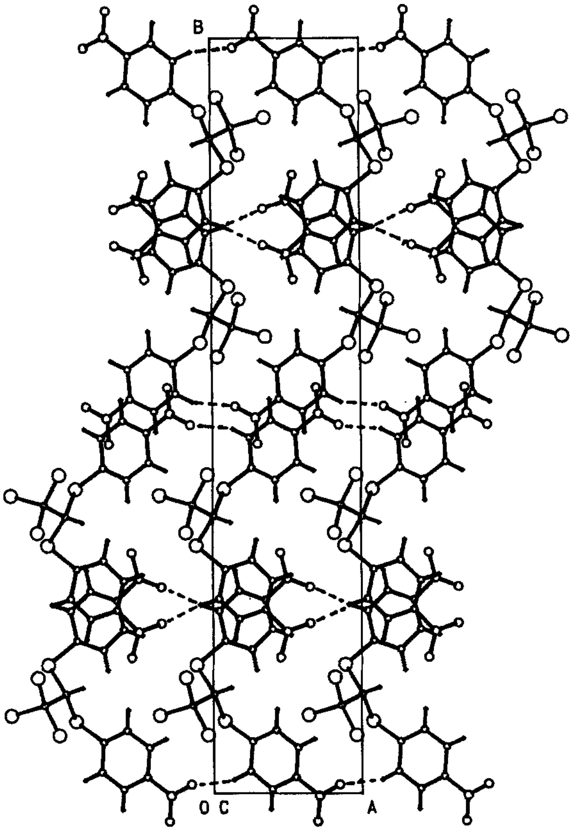

Fig. 2. Packing diagram viewed down ZO.

et al., 1978). In these structures also the pairs of angles S—C_{Ar}—C_{Ar} are usually unequal. Values (deg) are 117.7 and 122.1 for both pairs for (**7**)* (space group C2, $Z = 2$); 119.7 and 121.4, 114.4 and 122.7 for (**9**)*; differences (deg) between the pairs of angles for (**8**) are 7,6,5,5,7, and 1 where the esd for the individual bond angles is 1 and the range of values is 115 to 125 (deg). [*Values are taken from the CSD (Allen *et al.*, 1979).]

A packing diagram is given in Fig. 2. Two short H · · · O distances are found. In each case the hydrogen atom is bonded to an aromatic ring. For C(12)—H(12) · · · O(12)′ [at $1 + x, y, z$ to O(12)] the C—H · · · O angle is 161.4(6) (deg), C · · · O is 3.42(1) (Å) and H · · · O is 2.50(1) (Å); for C(22)—H(22) · · · O(22)′ [at $1 + x, y, 1 + z$ to O(22)] the C—H · · · O angle is 159.2(7) (deg), C · · · O is 3.362(7) Å and H · · · O is 2.447(6) Å. These short H · · · O distances are shown in Fig. 2 by dashed lines.

Acknowledgments

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Anisotropic temperature and structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63147 (13 pages).