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Structure of 2-(*N*,*N*-Dimethyliminio)-2-phenyldithioacetate, a Probable Intermediate of the Willgerodt–Kindler Reaction

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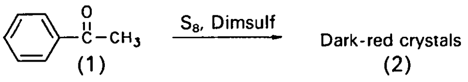
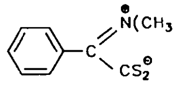
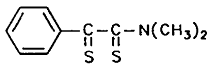
Abstract. $C_{10}H_{11}NS_2$, $M_r = 209.3$, orthorhombic, *Pbca*, $a = 11.662$ (1), $b = 11.709$ (1), $c = 15.430$ (1) Å, $V = 2107.0$ (3) Å^3, $Z = 8$, $D_x = 1.32$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 4.4$ cm^{-1}, $F(000) = 880$, $T = 293$ K, $R = 0.043$ for 1246 unique observed reflections. The structure of the title compound, a probable intermediate of the Willgerodt–Kindler reaction, was solved by direct methods. The observed molecular geometry confirms the postulated zwitterionic structure.

Introduction. In organic chemistry the Willgerodt–Kindler reaction has been known for a long time and successfully used to prepare ω-arylalkane carboxylic acids *via* their thioamides from aryl alkyl ketones with the same number of C atoms (Krauch & Kunz, 1976). The mechanism of this reaction is rather complicated and despite much experimental work it has not been elucidated until now. As a primary step the formation of a thioketone or a (multiple) thiolation of the methyl group are discussed in the literature (Wegler, Kühle & Schäfer, 1958; Asinger, Schäfer, Halcour, Saus & Triem, 1963). But all attempts to identify, let alone to isolate, corresponding intermediates were without success. The function of hydrogen sulfide as a redox mediator is common to most of the mechanistic considerations (Mayer & Funk, 1963). Therefore, the isolation of potential intermediate products of the Willgerodt–Kindler reaction may possibly succeed if the hydrogen sulfide formed by the thiolation of the aryl methyl ketone is quickly removed from the reaction mixture after its formation. This assumption was confirmed by the observation that the thiolation of acetophenone gives a dark-red crystalline product (2) in the presence of dimsulf, *i.e.* the distillable 1:1 addition compound of dimethylamine and sulfur dioxide which binds hydrogen sulfide immediately and completely. Because (2) reacts with hydrogen sulfide giving sulfur and the Willgerodt–Kindler product *N*,*N*-dimethylphenylthioacetamide, it may be justly assumed to be an intermediate. Consequently, the constitution and structure of (2) was of particular interest. Based on the results of elemental analysis, some spectroscopic investigations and chemical intuition the isomeric structures (2*a*) to (2*d*) came into consideration. In order to reach an unequivocal decision an X-ray analysis of (2) has been performed.

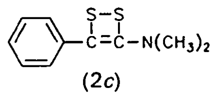




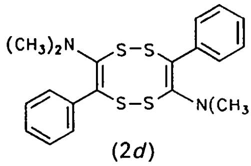
(2*a*)



(2*b*)



(2*c*)



(2*d*)

Experimental. Dark red crystals of the title compound (2*a*) were obtained by recrystallization from methanol. X-ray measurements were performed on a Stoe Stadi-4 diffractometer for a crystal with dimensions 0.25 × 0.25 × 0.15 mm, using graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were derived from the setting angles for 72 reflections in the 2θ range 20.0–28.0°. Intensity-data measurement: ω–θ scan, $2\theta_{\max} = 45°$; *hkl* range $-12/12$, $-12/12$, $-16/16$ for the *hkl* and $-h$, $-k$, $-l$ octants; 3816 reflections measured, 1358 unique

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Table 1. *Final fractional coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.04218 (7)	0.72646 (7)	0.37391 (6)	0.0589 (3)
S2	−0.04809 (7)	0.91117 (6)	0.25419 (5)	0.0507 (3)
N1	−0.2431 (2)	0.7193 (2)	0.3361 (1)	0.0380 (8)
C1	−0.0561 (3)	0.8108 (2)	0.3301 (2)	0.0376 (10)
C2	−0.1737 (2)	0.7974 (2)	0.3672 (2)	0.0343 (10)
C3	−0.2100 (4)	0.6481 (3)	0.2610 (3)	0.054 (1)
C4	−0.3575 (3)	0.6934 (3)	0.3721 (3)	0.046 (1)
C5	−0.2081 (2)	0.8763 (2)	0.4368 (2)	0.0330 (10)
C6	−0.3098 (3)	0.9383 (3)	0.4317 (2)	0.043 (1)
C7	−0.3351 (3)	1.0200 (3)	0.4941 (2)	0.053 (1)
C8	−0.2604 (4)	1.0400 (3)	0.5605 (2)	0.058 (1)
C9	−0.1594 (3)	0.9800 (3)	0.5659 (2)	0.057 (1)
C10	−0.1324 (3)	0.8987 (3)	0.5044 (2)	0.045 (1)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

C1—C2	1.495 (4)	C2—N1	1.311 (3)
C1—S1	1.657 (3)	C3—N1	1.478 (4)
C1—S2	1.662 (3)	C4—N1	1.477 (4)
C2—C5	1.473 (4)		
C2—C1—S1	114.6 (2)	C2—C5—C6	121.1 (2)
C2—C1—S2	113.3 (2)	C2—C5—C10	119.5 (2)
S1—C1—S2	132.1 (1)	C2—N1—C3	121.2 (2)
C1—C2—C5	117.6 (2)	C2—N1—C4	124.3 (2)
C1—C2—N1	120.0 (2)	C3—N1—C4	114.5 (2)
C5—C2—N1	122.4 (2)		
S1—C1—C2—C5	95.1 (3)	N1—C2—C5—C6	−50.4 (3)
S1—C1—C2—N1	−86.6 (3)	N1—C2—C5—C10	136.5 (3)
S2—C1—C2—C5	−83.1 (2)	C1—C2—N1—C3	−3.7 (3)
S2—C1—C2—N1	95.2 (2)	C1—C2—N1—C4	175.4 (3)
C1—C2—C5—C6	127.9 (3)	C5—C2—N1—C3	174.5 (3)
C1—C2—C5—C10	−45.3 (3)	C5—C2—N1—C4	−6.4 (3)

($R_{int} = 0.015$), 1246 reflections with $I \geq 2\sigma(I)$ considered observed and used in the structure refinement. Three standard reflections (402, $\bar{4}02$, 342) varied in intensity by 4.8, 3.8 and 5.6%, respectively. Lp corrections were carried out but absorption effects were ignored. The structure was solved by direct methods and refined on F by full-matrix least-squares procedures with anisotropic displacement parameters for all non-H atoms. All H-atom positions were located in a difference Fourier map and isotropically refined. The final weighting scheme was $w = 2.07/\sigma^2$; an empirical extinction correction was applied with $F_{corr} = F_c(1 - \chi F_c^2/\sin\theta)$ [χ refined to $5.52\,(7) \times 10^{-7}$]. The refinement converged to final $R = 0.043$, $wR = 0.028$, $S = 4.83$ for 7.64 reflections per refined parameter. The final difference map showed maximum and minimum heights of 0.21 and −0.22 e Å^{-3}, respectively. The maximum Δ/σ in the last refinement cycle was 0.004. Atomic scattering factors were obtained from *SHELX76* (Sheldrick, 1976). All calculations and plots were performed with the program packages *SHELX76*, *SHELXS86* (Sheldrick, 1986), *EDIT* (Jaskólski, 1982) and *ORTEPII* (Johnson, 1976).

Discussion. Final positional parameters and U_{eq} values for non-H atoms are given in Table 1.* Selected bond lengths, bond angles and torsion angles are listed in Table 2. The atomic numbering scheme is shown in Fig. 1.

The observed geometric bond parameters establish the characterization of (2*a*) as a zwitterion. Both atoms N1 and C2 are sp^2 hybridized with bond-angle sums of 360.1 and 360.0°, respectively, and the bond length N1—C2 [1.311 (3) Å] approaches the standard value for a true N═C double bond [1.29 Å (Rademacher, 1987)]. The C—S bond distances do not

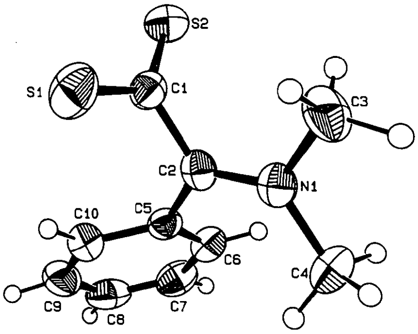

Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radius.

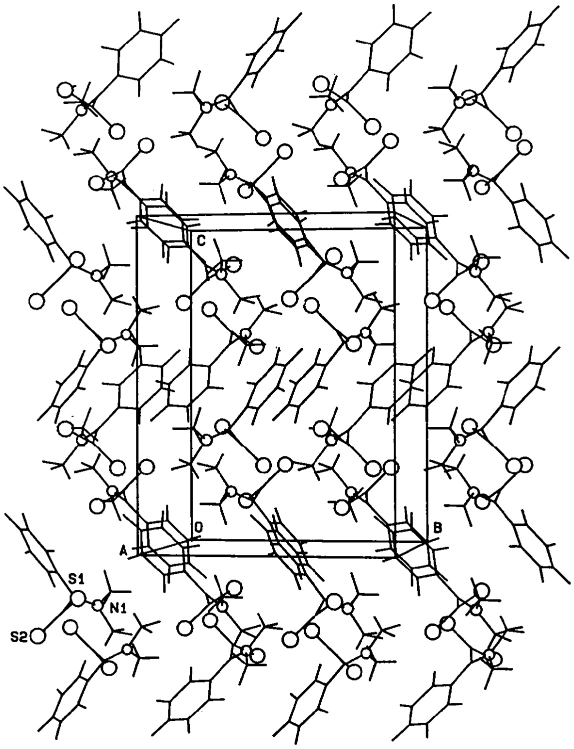

Fig. 2. Molecular packing.

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* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55389 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

differ significantly. They lie considerably below the range for C—S single bonds [1.76–1.83 Å (Rademacher, 1987)] but agree completely with the values 1.659 (2) and 1.666 (2) Å observed in the related zwitterionic compound $S_2C—C[N(CH_3)_2]_2$ (Ziegler, Weber, Nuber & Serhadle, 1987). The same is true for the N—C(methyl) distances which correspond clearly to single bonds. The C1—C2 bond length [1.495 (3) Å] is a little shorter than the average of experimental values for carboxylic anions [1.520 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. The dithioacetate fragment is planar; the only significant deviation from the plane through its four atoms is 0.014 (2) Å for C1. It is tilted to the exactly planar formamidine group $C=N(CH_3)_2$ by 87.6°. The benzene ring has standard dimensions [C—C = 1.382 (11) Å, C—C—C = 120.0 (5)°]. The angle between its plane and the approximately planar fragment defined by atoms C1···C5 and N [with maximum deviations from the least-squares plane of 0.084 (4) Å for C3 and 0.066 (3) Å for C4] amounts to 49.3°.

The molecular packing of (2*a*) is shown in Fig. 2. All intermolecular contacts are consistent with van der Waals radii.

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Structure of *p*-Acetylbenzoic Acid Oxime

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Abstract. 4-(1-Hydroxyiminoethyl)benzoic acid, $C_9H_9NO_3$, $M_r = 179.18$, orthorhombic, *Pbca*, $a = 7.137\,(1)$, $b = 14.438\,(3)$, $c = 16.110\,(3)$ Å, $V = 1660.0\,(5)$ Å^3, $Z = 8$, $D_x = 1.434$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.02$ cm^{-1}, $F(000) = 752$, $T = 295$ K, $R = 0.0474$, $wR = 0.0493$, for 1268 reflections [$|F| > 3.92\sigma(F)$]. The structure is formed from infinite polar chains of molecules held together by pairs of strong hydrogen bonds between the carboxyl and oxime groups. There are no strong interactions between the approximately antiparallel chains.

Introduction. As part of a study of molecules that crystallize in space groups with polar axes (Curtin & Paul, 1981), the crystal structure of (−)-(1*S*)-pinonic acid *β*-oxime was determined in our laboratory (Padmanabhan, Paul & Curtin, 1989). The packing was dominated by chains of pinonic acid oxime molecules held together by hydrogen bonds between the carboxyl and oxime groups. In an attempt to establish how generally this type of hydrogen bonding occurs, we have determined the crystal structures of several molecules containing both the carboxyl and oxime groups. In this paper, we report the structure of *p*-acetylbenzoic acid oxime.

Experimental. The title compound was synthesized by the reaction of *p*-acetylbenzoic acid with

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