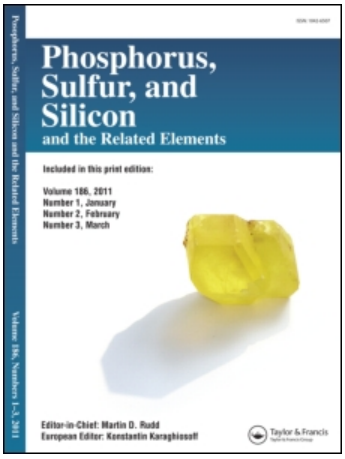


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ARYL THIOCARBAMOYLATIONS OF PHTHALIDES AND X-RAY STUDIES OF THREE REACTION PRODUCTS

Wolfgang Dölling[a]; Thomas Gildenast[a]; Matthias Biedermann[b]; Helmut Hartung[b]
[a] Martin Luther University Halle-Wittenberg, Institute of Organic Chemistry, Halle, Saale [b] Institute of Physical Chemistry, Mühlpforre 1, Halle, Saale, Germany

To cite this Article Dölling, Wolfgang , Gildenast, Thomas , Biedermann, Matthias and Hartung, Helmut(1996) 'ARYL THIOCARBAMOYLATIONS OF PHTHALIDES AND X-RAY STUDIES OF THREE REACTION PRODUCTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 116: 1, 185 — 202
To link to this Article: DOI: 10.1080/10426509608040479
URL: http://dx.doi.org/10.1080/10426509608040479

Phosphorus, Sulfur, and Silicon, 1996, Vol. 116, pp. 185–202
Reprints available directly from the publisher
Photocopying permitted by license only

ARYL THIOCARBAMOYLATIONS OF PHTHALIDES AND X-RAY STUDIES OF THREE REACTION PRODUCTS

WOLFGANG DÖLLING[a,*], THOMAS GILDENAST[a], MATTHIAS BIEDERMANN[b] and HELMUT HARTUNG[b]

[a]*Martin Luther University Halle-Wittenberg, Institute of Organic Chemistry, Kurt-Mothes-Straße 2, D-06120 Halle (Saale);* [b]*Institute of Physical Chemistry, Mühlpforte 1, D-06108 Halle (Saale), Germany*

(Received 16 April 1996; In final form 7 May 1996)

Phthalides **1** have been thiocarbamoylated. We were able to isolate and characterize different reaction products formed by treatment of a mixture of **1** and phenyl isothiocyanate with various amounts of base. 3-Oxo-1,3-dihydro-isobenzofuran-1-carbothioic acid phenylamide **3**, 3-{[(1-oxo-3H-isobenzofuranylidene)-phenylamino-methylenethio]methylthio-phenylamino-methylene}-3H-isobenzofuran-1-one **4**, 3-oxo-N,1-diphenyl-1,3-dihydro-isobenzofuran-1-carboximidothioic acid methyl ester **5**, 3-alkylthio-4-hydroxy-2-phenyl-2H-isoquinolin-1-one **6**, and 3-oxo-N,N-diphenyl-3H-isobenzofuran-1,1-dicarboximidothioic acid dimethyl ester **7** were obtained. X-ray studies have been performed in order to identify unequivocally the reaction products.

Keywords: Phthalides; aryl thiocarbamoylation; 3-oxo-1,3-dihydro-isobenzofuran-1-carbothioic acid phenylamide; x-ray analysis

INTRODUCTION

We are interested in reactions of α-oxygen substituted C-nucleophiles with sulfur containing heterocumulenes. Our first results in this field were recently published in two papers.[1,2] In order to better understand these processes promoted by heteroatomic substituents phthalides **1** have been studied. These compounds represent in the deprotonated form integrated α-oxygen substituted C-nucleophiles with a phenylene group between the electron withdrawing car-

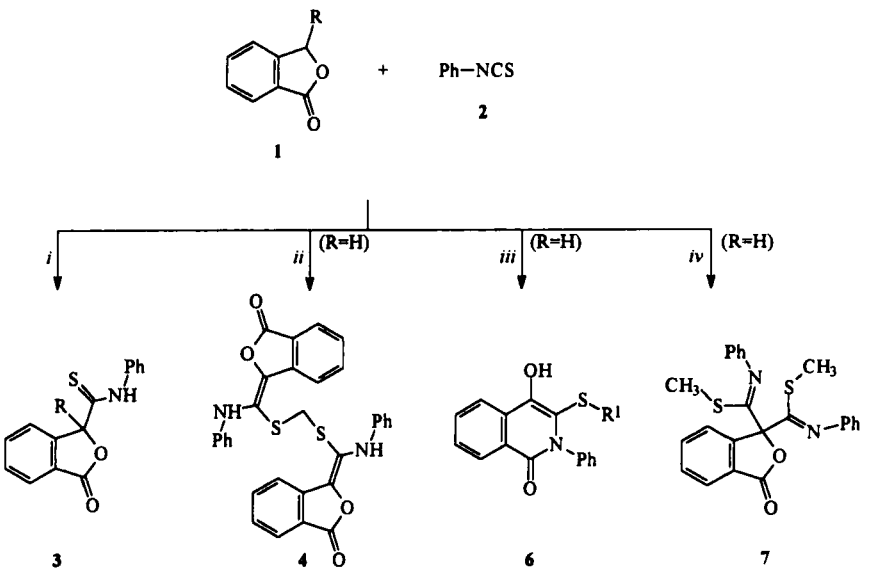
*Corresponding author.

bonyl function and the (in the phthalide weakly acidic) methylene group. The aim of our investigations was to clarify whether the electrophilic heterocumulene attacks the carbon- or the oxygen-nucleophile. The latter should be also possible according to the mesomeric description of the deprotonated phthalide molecule. We wish to report in this paper on the different products formed according to the amount of base and alkyl halides used.

RESULTS AND DISCUSSION

The methylene group of phthalides has been recognized to be CH-acidic already some time ago and various base-catalyzed aldol and Dieckmann condensations have been reported. In the deprotonated form it may be effectively attacked by electrophiles.[3–11] Other corresponding reactions are described in the literature.[12–17] Phthalide reacts for example in the sense of an aldol condensation with aldehydes,[12,13] it can give a self condensation,[15] and by ester condensations phthalidylketones[14] are formed. Furthermore, the phthalide enolate adds to Schiff's bases and the resulting intermediate cyclizes to a mixture of *cis*- and *trans*-isoquinolinones.[18] The oxygen atom of the enolate may be silylated in the case of 3-arylphthalides.[19] Annulation reactions based on addition of stabilized phthalide anions to α,β-unsaturated systems have been also reported.[20] This reaction involves the combination of a Michael addition followed by a Claisen condensation.

In a review article[21] the use of isothiocyanates in syntheses with particular consideration of heterocycles has been described. Numerous C-nucleophiles react with isothiocyanates.[22–28] But there are only a few reports about the reactions of these compounds with α-heteroatom substituted carbanions.[29] The reaction of isothiocyanates with CH-acidic compounds in basic medium represents the general way to ketene-N,S-acetals.[30] But in our case we were not able to isolate such compounds starting with the phthalide system except for **4**. However, the reaction with 1 equiv. base gave thioanilides **3** after acidification in 40–64% yield. The assigned structure of products **3** is supported by spectral and analytical data. All efforts to synthesize ketene N,S-acetals like **4** were unsuccessful. Compound **4** was obtained by reaction of an equimolar mixture of phthalide, base, and methylene iodide as the product of intermolecular alkylation. Other substances were surprisingly isolated instead of the expected ones when the enolates of **1**, which are generated by treating the appropriate phthalide with two equiv. of a strong base (i.e. potassium *tert*-butoxide), have been caused to react with phenyl isothiocyanate (Scheme 1).



3	R
a	H
b	CH_3
c	C_6H_5

6	R^1
a	CH_3
b	$CH_2COC_6H_5$
c	$CH_2COC_6H_4$-4-Br
d	$CH_2COC_6H_4$-4-NO_2
e	$CH_2COC(CH_3)_3$

SCHEME 1 Conditions: *i)* KO-^{t}Bu/H^+, *ii)* KO-^{t}Bu/0.5 equiv. CH_2I_2, *iii)* KO-^{t}Bu/R^1Hal (Hal=Br, I), *iv)* KO-^{t}Bu/TMSCl/KO-^{t}Bu/PhNCS/2 CH_3I.

Treatment of freshly sublimated **1** (R=H) with phenyl isothiocyanate under basic conditions (2 equivalents of base) followed by an alkylating agent gave substituted 4-hydroxy-2-phenyl-2H-isoquinolin-1-ones **6a–e**. These compounds, of which only a few examples have been reported till now,[31–33] were isolated and fully characterized. In the case of the formation of **6a** by methylation with methyl iodide compound **7** was detected as a by-product by High Performance Thin Layer Chromatography (HPTLC). This is shown in Fig. 1. The assignment of the different spots was made according to the chosen standard without quantification. 4-Hydroxy-isoquinolinones **6a**, **6b** are very well separated from the thioanilides **3a**, **3b** and compound **7**. The structure of **7** has been proved by X-ray analysis.

The formation of 4-hydroxy-2-phenyl-2H-isoquinolin-1-ones **6** is believed to proceed *via* reactive dianion, which is obtained by treatment of **1** and **2** with two equivalents of potassium *tert*-butoxide and cyclocondensation, or *via* ring trans-

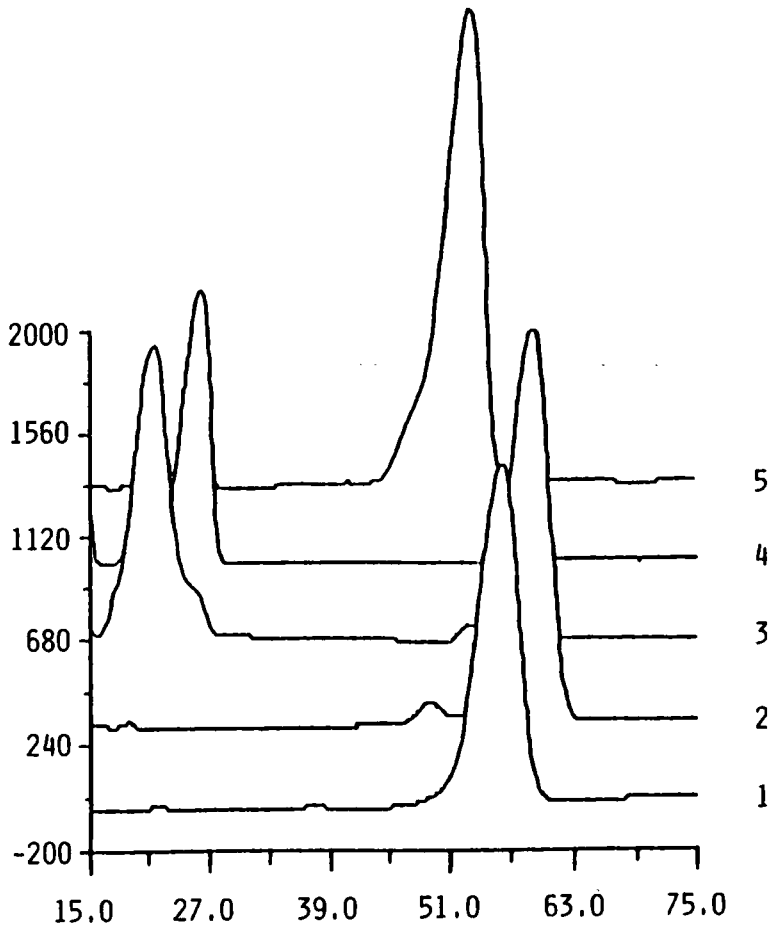


FIGURE 1 HPTLC of the standard test mixture: trace 1 = **3a**, trace 2 = **3b**, trace 3 = **6a**, trace 4 = **6b**, trace 5 = **7**; stationary phase: plates of silicagel 60 (MERCK, 5μm, 0.2 mm); mobile phase: chloroform/*n*-hexane 9:1; detection: UV 220 nm; sample mass: 20 μg.

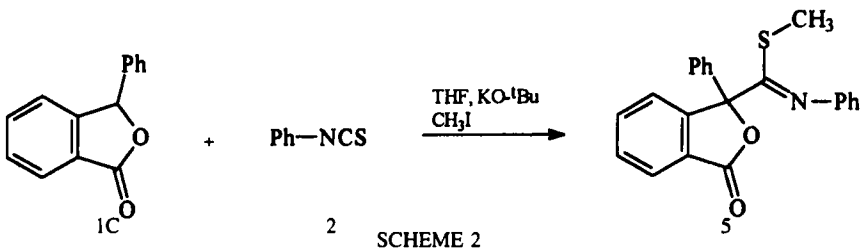
formation, respectively. Obviously, the possibility of a better stabilisation by amide creation is important for the found results.

The formation of compound **7** will be the main reaction in presence of chlorotrimethylsilane, 2 equiv. base, and 2 equiv. MeI.

The synthesis of compound **7** shows that phenyl isothiocyanate can attack the enolate two times. This result is comparable with that found recently in the reaction of 2-methyl-pyridine with this reagent.[34]

The reaction pathways show that the electrophilic heterocumulene attacks the carbon- and not the oxygen-nucleophile. The latter should be also possible in the mesomeric description of the deprotonated phthalide.

The reaction of 3-phenyl-phthalide **1c** leads to 3-oxo-N,1-diphenyl-1,3-dihydro-isobenzofuran-1-carboximidothioic acid methyl ester **5** independently of the applied amount of base (Scheme 2).



SCHEME 2

Indeed, in this example neither rearrangement or ring transformation nor formation of thioanilide was detected.

Crystal and Molecular Structures of Compounds *3a, 6a* and *7*

X-ray analyses using single crystals of compounds **3a**, **6a** and **7** have been performed mainly for the purpose of an unequivocal identification of these reaction products. Their findings prevented misinterpretations of reaction courses and provided essential evidence for the correctness of the results summarized in scheme 1. Moreover, an X-ray analysis enables a complete and accurate structural characterization of the investigated compound and thus it may contribute to a better understanding of the reactivity of chemical species and the elucidation of reaction pathways. From this point of view some details of the observed structures will be discussed in the following.

The molecular structures of **3a**, **6a** and **7** are shown in figure 2. Selected bond lengths and angles are listed in tables I and II.

Compounds **3a** and **7** have the isobenzofuran structural fragment in common. For the sake of good comparability an appropriate atomic numbering have been applied. In both structures the bicyclic ring system is planar in good approximation. The maximum deviation from the corresponding l.s. plane amounting to 0.026(2) Å for C1 in **3a** is probably caused by the steric demand on this atom also indicated by the rather great difference of 5.1° for the angle O1-C1-C9 compared in **3a** and **7**. According to the different bonding situation within the C1-C9-N1-C10 bridge the interplanar angle between the isobenzofuran fragment and the phenyl ring C10···C15 is quite different in both compounds being

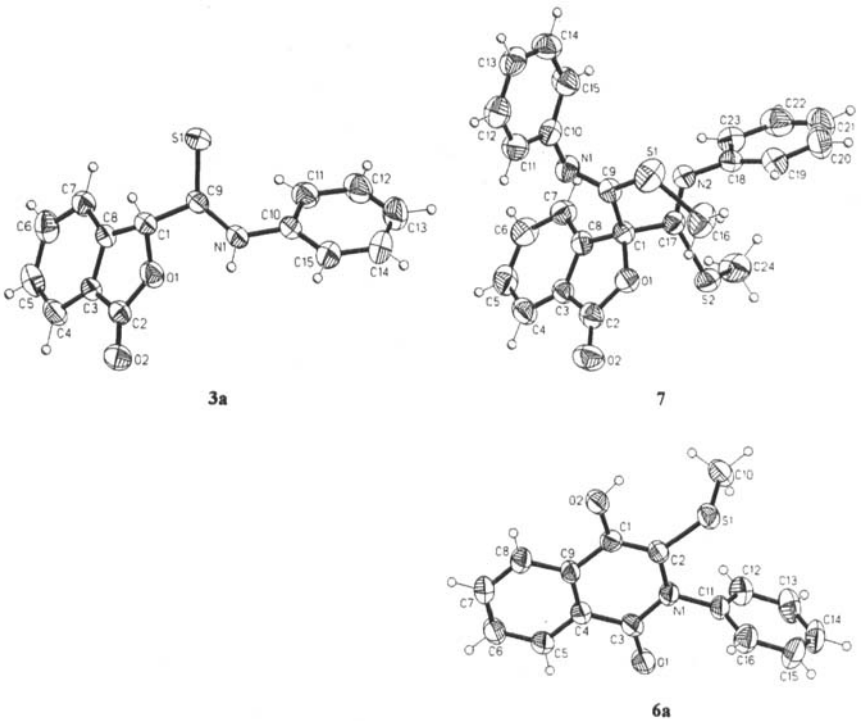


FIGURE 2 Molecular structure of compounds **3a**, **6a** and **7**. Displacement ellipsoides are drawn at the 50% probability level; H atoms are represented by small circles of arbitrary size.

124.8(1)° in **3a** and 79.6(1)° in **7**. The observed N1-C9 bond length of 1.327(2) Å in **3a** is markedly shorter than the standard value of 1.43 Å given for a $C(sp^2)$-$N(sp^3)$ bond and only a little longer than the value of 1.29 Å for a $C(sp^2)$=$N(sp^2)$ double bond.[35] Furthermore, the four atoms S1, N1, C1, and C9 are exactly in a common plane within experimental error and the S1-C9 bond is with 1.654(1) Å near the standard value of 1.63 Å for a C=S double bond. All these findings suggest a significant contribution of the zwitterionic resonance structure to the description of the thioamide structural fragment. A suitable object of comparison is 2-picoline-α,α-bis(N-4-tolylthiocarboxamide). In its molecular structure bond lengths of 1.331(2) and 1.377(2) Å for C-N and 1.664(2) and 1.635 Å for C=S were observed.[34] These data are in good agreement with the corresponding ones in **3a**.

In **7** the bond lengths N1-C9 = 1.264(3) Å and N2-C17 = 1.263(2) Å are in best agreement with each other and can be classified as true double bonds. Surprisingly, the two chemically equivalent bonds S1-C9 and S2-C17 differ only

TABLE I Selected bond lengths (Å) and angles (°) of **3a** and **7**

Atoms	*3a*	*7*	*Atoms*	*3a*	*7*
S1-C9	1.654(1)	1.760(2)	C3-C8	1.385(2)	1.373(3)
S1-C16		1.793(3)	C4-C5	1.372(2)	1.377(3)
S2-C17		1.776(2)	C5-C6	1.387(2)	1.381(3)
S2-C24		1.800(3)	C6-C7	1.386(2)	1.380(3)
O1-C1	1.449(2)	1.452(2)	C7-C8	1.382(2)	1.379(3)
O1-C2	1.369(2)	1.386(2)	C10-C11	1.384(2)	1.383(3)
O2-C2	1.202(2)	1.193(3)	C10-C15	1.382(2)	1.386(3)
N1-C9	1.327(2)	1.264(3)	C11-C12	1.389(2)	1.377(3)
N1-C10	1.429(2)	1.425(3)	C12-C13	1.366(3)	1.374(3)
N1-H1N1	0.85(2)		C13-C14	1.376(3)	1.367(3)
N2-C17		1.263(2)	C14-C15	1.391(2)	1.388(3)
N2-C18		1.422(3)	C18-C19		1.376(3)
C1-C8	1.507(2)	1.514(3)	C18-C23		1.390(3)
C1-C9	1.521(2)	1.532(3)	C19-C20		1.387(3)
C1-C17		1.531(3)	C20-C21		1.365(4)
C2-C3	1.465(2)	1.465(3)	C21-C22		1.372(4)
C3-C4	1.388(2)	1.386(3)	C22-C23		1.382(3)
C9-S1-C16		108.0(1)	C8-C3-C4	121.9(1)	121.7(2)
C17-S2-C24		104.5(1)	C8-C3-C2	108.6(1)	109.1(2)
C2-O1-C1	110.8(1)	110.9(2)	C4-C3-C2	129.5(1)	129.2(2)
C9-N1-C10	128.4(1)	120.4(2)	C5-C4-C3	117.4(1)	117.2(2)
C9-N1-H1N1	116(1)		C4-C5-C6	120.8(1)	121.1(2)
C10-N1-H1N1	115(1)		C7-C6-C5	121.9(2)	121.4(2)
C17-N2-C18		123.5(2)	C8-C7-C6	117.3(1)	117.6(2)
O1-C1-C8	104.2(1)	103.7(2)	C7-C8-C3	120.6(1)	120.9(2)
O1-C1-C9	112.1(1)	107.0(2)	C7-C8-C1	131.2(1)	130.4(2)
O1-C1-C17		110.0(2)	C3-C8-C1	108.1(1)	108.7(2)
C8-C1-C9	114.2(1)	112.8(2)	N1-C9-C1	115.3(1)	117.6(2)
C8-C1-C17		109.4(2)	N1-C9-S1	128.4(1)	120.9(2)
C9-C1-C17		113.5(2)	C1-C9-S1	116.3(1)	121.4(2)
O2-C2-O1	121.1(1)	120.6(2)	N2-C17-C1		116.1(2)
O2-C2-C3	130.7(1)	131.8(2)	N2-C17-S2		130.9(2)
O1-C2-C3	108.2(1)	107.6(2)	C1-C17-S2		112.9(1)

slightly but significantly by 0.016 Å. Apart from that, they agree well with the standard length of 1.76 Å for an S-C(sp^2) single bond.[35]

A short N1...O1 contact distance indicates the existence of an intramolecular hydrogen bond in **3a**. Its geometry is characterized by the following data: N1...O1 2.657(2), N1-H1 0.85(2), O1...H1 2.20(2) Å, N1-H1...O1 114(1)°. According to a model developed by Jaskólski[36] this H bond can be classified as to be of medium strength. Apparently it has an influence on the molecular conformation of **3a** and is responsible for the flattening of the structural fragment consisting of atoms C1, C9, N1, O9 (maximum deviation from the l.s. plane: 0.072(1) Å for C9). An also relatively short intermolecular contact dis-

TABLE II Selected bond lengths (Å) and angles (°) of **6a**

Atoms		*Atoms*		*Atoms*	
S1-C2	1.754(3)	C1-C2	1.347(3)	C8-C9	1.411(3)
S1-C10	1.801(3)	C1-C9	1.448(3)	C11-C12	1.366(3)
O1-C3	1.240(3)	C3-C4	1.468(3)	C11-C16	1.372(4)
O2-C1	1.356(3)	C4-C5	1.403(4)	C12-C13	1.387(4)
O2-H1O2	0.82	C4-C9	1.388(4)	C13-C14	1.359(4)
N1-C2	1.417(3)	C5-C6	1.369(3)	C14-C15	1.365(4)
N1-C3	1.379(3)	C6-C7	1.389(4)	C15-C16	1.373(4)
N1-C11	1.457(3)	C7-C8	1.373(4)		
C2-S1-C10	103.0(1)	O1-C3-N1	120.7(2)	C4-C9-C1	118.8(2)
C1-O2-H1O2	109.5(1)	O1-C3-C4	123.5(2)	C8-C9-C1	122.2(3)
C3-N1-C2	123.4(2)	N1-C3-C4	115.8(2)	C12-C11-C16	120.4(2)
C3-N1-C11	115.4(2)	C9-C4-C5	120.2(2)	C12-C11-N1	120.3(2)
C2-N1-C11	121.2(2)	C9-C4-C3	121.4(2)	C16-C11-N1	119.3(2)
C2-C1-O2	124.8(2)	C5-C4-C3	118.5(3)	C11-C12-C13	119.2(3)
C2-C1-C9	120.6(3)	C6-C5-C4	120.4(3)	C14-C13-C12	120.5(3)
O2-C1-C9	114.6(2)	C5-C6-C7	119.3(3)	C13-C14-C15	119.8(3)
C1-C2-N1	120.0(2)	C8-C7-C6	121.5(2)	C14-C15-C16	120.5(3)
C1-C2-S1	121.1(2)	C7-C8-C9	119.6(3)	C11-C16-C15	119.6(3)
N1-C2-S1	118.9(2)	C4-C9-C8	119.0(2)		

tance of 2.971(2) Å between N1 and O2 (symmetry code: 1-x, 2-y, -z) can be interpreted as hint at a weak hydrogen bond in the crystal lattice of **3a**. A summary of selected bond lengths and angles of **3a** and **7** is given in Table I.

The bicyclic isoquinoline ring system in **6a** has a high degree of planarity (maximum deviation from the l.s. plane: 0.030(3) Å for C9). It is inclined to the exactly planar phenyl ring by 87.2(1)°. The N1-C11 distance of 1.457(3) Å is rather long compared with the standard value of 1.40 Å for an $N(sp^2)$-$C(sp^2)$ single bond.[35] A short intermolecular contact distance O2...O1 (symmetry code: x, 1+y, z) of 2.717(3) Å indicates an intermolecular hydrogen bond in the crystal lattice of **6a**, too. A summary of selected bond lengths and angles of **6a** is given in Table II.

EXPERIMENTAL

All reactions were carried out under argon or nitrogen atmosphere. Melting points were determined on a Kofler hot stage microscope and are uncorrected. Infrared spectra were measured in nujol with an IR-spectrophotometer Specord Carl Zeiss Jena and are given in cm^{-1}. ^1H and ^{13}C nmr spectra were recorded on either a BRUKER WP 200, AC 80 or a VARIAN Gemini 200 and Unity 500 spectrometer in $CDCl_3$ or DMSO-d_6. The chemical shifts are reported in parts

per million (ppm) downfield from internal tetramethylsilane. Mass spectra were measured on an AMD 402 of the AMD Intectra GmbH. HPTLC: TLC-Applicator AS 30 and Densitometer CD 60 of Desaga.

3-Oxo-1,3-dihydro-isobenzofuran-1-carbothioic acid phenylamide 3a (R=H)

Potassium *tert.* butoxide (1.12 g, 10 mmol) was added to a solution of phthalide **1** (R=H, 1.34 g, 10 mmol) and phenyl isothiocyanate **2** (1.35 g, 10 mmol) in dry THF (40 ml) at −78°C. After the addition, the mixture was stirred for 2 h and HCl (12%, 40 ml) was added dropwise. The resulting solution was stirred 10 min, after removing of the cooling bath it was warmed up to room temperature and stirred for 5 h. The crude product precipitated was filtered off by suction and recrystallized from ethanol. Yield: 1.15 g (42.8%); m.p.: 174–6 °C; IR: 3260 (νNH), 1765 (νC=O), 1590, 1530, 1490, 1460, 1380, 1280, 1260, 1200, 1180, 1140, 1120, 1090, 1050, 1000, 970, 950, 900, 765, 730, 700, 690. ^{1}H-NMR (200 MHz; $CDCl_3$): 6.27 (s, 1H, OCH); 7.21–7.89 (m, 8H, aromat.); 8.28 (d, 1H, aromat.); 9.71 (br. s., 1H, NH, disappears on treatment with D_2O); ^{13}C-NMR (50 MHz; $CDCl_3$): 84.8 (OCH); 123.5; 123.7; 124.7; 125.5; 127.4; 128.9; 130.3; 134.8; 137.1; 145.9 (C=$C_{aromat.}$); 169.2 (C=O); 192.6 (C=S); MS (%): m/e = 269 ($M^{+\cdot}$, 18); 236 ([M-·SH]$^+$, 4); 136 ([C_6H_5NHCS]$^{+\cdot}$, 26); 134 ([M-C_6H_5NHCSH]$^{+\cdot}$, 100); 77 ([C_6H_5]$^+$, 31). $C_{15}H_{11}NO_2S$ (269.3) requires C, 66.89; H, 4.11; N, 5.20; S, 11.91. Found: C, 66.91; H 4.24; N, 5.02; S, 12.15%.

1-Methyl-3-oxo-1,3-dihydro-isobenzofuran-1-carbothioic acid phenylamide 3b (R=CH_3)

Potassium *tert.* butoxide (2.2 g, 19.6 mmol) was added to a solution of 3-methylphthalide[37] **1** (R=CH_3, 2.9 g, 19.6 mmol) and phenyl isothiocyanate **2** (2.65 g, 19.6 mmol) in dry THF (40 ml) at −78 °C. After the addition, the mixture was stirred for 2.5 h and HCl (3%, 40 ml) was added dropwise. The resulting solution was stirred several hours at RT. The organic phase was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed twice with water, dried over sodium sulphate and concentrated to give a solid which can be recrystallized from ethanol. Yield: 2.2 g (39.6%); m.p.: 126–8 °C; IR: 3325 (νNH), 1765 (νC=O), 1590, 1510, 1460, 1375, 1280, 1260, 1150, 1110, 1060, 1010, 1000, 910, 765, 750, 700; ^{1}H-NMR (200 MHz; $CDCl_3$): 2.15 (s, 3H, CH_3); 7.13–7.86 (m, 8H, aromat.); 8.28 (d, 1H, aromat.); 9.89 (s, 1H, NH); ^{13}C-NMR (20 MHz; $CDCl_3$): 29.6

(CH_3); 91.9 ($OC_{quart.}$); 123.6; 124.0; 125.1; 125.5; 127.4; 129.0; 130.1; 134.6; 137.9; 150.7 ($C{=}C_{aromat.}$); 168.6 (C=O); 197.7 (C=S); MS (%): m/e = 283 ($M^{+\cdot}$, 9); 148 ($[M\text{-}C_6H_5NCS]^{+\cdot}$, 100); 136 ($[C_6H_5NHCS]^{+\cdot}$, 9); 91($[C_7H_7]^+$, 10); 77 ($[C_6H_5]^+$, 25). $C_{16}H_{13}NO_2S$ (283.3) requires C, 67.82; H 4.62; N, 4.94; S, 11.32. Found: C, 68.36; H, 4.65; N, 4.87; S, 11.24%.

3-Oxo-1-phenyl-1,3-dihydro-isobenzofuran-1-carbothioic acid phenylamide 3c (R=C_6H_5)

Potassium *tert.* butoxide (1.12 g, 10 mmol) was added to a solution of 3-phenylphthalide[38] **1** (R=C_6H_5, 2.1 g, 10 mmol) and phenyl isothiocyanate **2** (1.35 g, 10 mmol) in dry THF (40 ml) at −78 °C. After the addition, the mixture was stirred for 2.5 h and HCl (3%, 40 ml) was added dropwise. The resulting solution was stirred several hours at RT. The precipitate formed was filtered off with suction and recrystallized from ethanol/acetone (1 : 1). Yield: 2.2 g (63.8%); m.p.: 155–6 °C; IR: 3265 (νNH), 1760 (νC=O), 1590, 1520, 1490, 1460, 1375, 1280, 1240, 1150, 1100, 1075, 1000, 970, 955, 930, 900, 800, 755, 745, 720, 690; ^{1}H-NMR (200 MHz; $CDCl_3$): 7.23–7.92 (m, 13H, aromat.); 8.44 (d, 1H, aromat.); 10.21 (s, 1H, NH); ^{13}C-NMR (20 MHz; $CDCl_3$): 94.0 ($OC_{quart.}$); 123.9; 124.8; 125.6; 127.0; 127.5; 127.7; 128.7; 129.1; 130.4; 134.5; 137.7; 139.3; 148.3 ($C{=}C_{aromat.}$); 168.2 (C=O); 195.9 (C=S); MS (%): m/e = 345 ($M^{+\cdot}$, 2); 210 ($[M\text{-}C_6H_5NCS]^{+\cdot}$, 100); 136 ($[C_6H_5NHCS]^{+\cdot}$, 20); 77 ($[C_6H_5]^+$, 41). $C_{21}H_{15}NO_2S$ (345.4) requires C, 73.02; H, 4.38; N, 4.06; S, 9.28. Found C, 73.08; H, 4.09; N, 3.81; S, 9.30%.

3-{[(1-Oxo-3H-isobenzofuranylidene)-phenylaminomethylenethio]methyl-thio-phenylamino-methylene}-3H-isobenzofuran-1-one 4

Potassium *tert.* butoxide (1.12 g, 10 mmol) was added to a solution of phthalide **1** (R=H, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (40 ml) at −78°C. After the addition, the mixture was stirred for 3 h and diiodomethane (2.68 g, 10 mmol) was added. The resulting solution was warmed up to room temperature and poured onto ice. The oily crude product separated was treated with petroleum ether to give a solid material which was recrystallized from ethanol and acetone. Yield: 0.8 g (29.0%; calc. as turnover of phthalide); m.p.: 215–217°C; IR (KBr): 3300 (νNH), 1750 (νC=O), 1630, 1600, 1500, 1475, 1460, 1430, 1350, 1310, 1290, 1270, 1180, 1100, 1030, 925, 770, 700; ^{1}H-NMR (200 MHz; DMSO-d_6): 3.65 (s, 1H, SCH_2); 3.96 (s, 1H, SCH_2); 6.75–8.53 (m, 18H, aromat.); 8.74 (s, 2H, NH); ^{13}C-NMR (50 MHz;

DMSO-d_6): 35.6 (SCH_2); 118.0; 120.3; 120.8; 122.4; 122.8; 124.4; 127.5; 128.6; 133.4; 135.2; 137.5; 141.8 (C═C, C═$C_{aromat.}$); 164.8 (C═O); MS (%): m/e = 550 ($M^{+\cdot}$, 57); 282 ([M-CH_2/2 + CH_2]$^{+\cdot}$, 82); 236 ([282-SCH_2]$^{+\cdot}$, 100); 133 ([C_6H_4COCOH]$^{+\cdot}$, 75); 104 ([C_6H_4CO]$^{+\cdot}$, 45); 77 ([C_6H_5]$^+$, 34). $C_{31}H_{22}N_2O_4S_2$ (550.6) requires C, 67.62; H, 4.03; N, 5.09; S, 11.65. Found C, 67.36; H 3.98; N 5.11; S, 10.97%.

3-Oxo-N,1-diphenyl-1,3-dihydro-isobenzofuran-1-carboximidothioic acid methyl ester 5

Potassium *tert.* butoxide (1.12 g, 10 mmol) was added with stirring to a solution of 3-phenylphthalide[38] **1** (R═C_6H_5, 2.1 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (40 ml) at −78 °C. After the addition, the mixture was stirred for 3 h and methyl iodide (1.42 g, 0.01 mol) was added dropwise. The resulting solution was warmed up to RT and stirred several hours at RT. The resulting mixture was poured onto ice (400 g). The precipitate formed was filtered off with suction and recrystallized from ethanol/acetone (1 : 1). Yield: 2.1 g (58.5%); m.p.: 124–5 °C; IR: 1780 (νC═O), 1600, 1590, 1480, 1465, 1375, 1290, 1260, 1210, 1140, 1100, 1070, 1000, 970, 870, 790, 770, 760, 750, 690; ^{1}H-NMR (200 MHz; $CDCl_3$): 2.06 (s, 3H, SCH_3); 6.79–7.90 (m, 14H, aromat.); ^{13}C-NMR (20 MHz; $CDCl_3$): 16.1 (SCH_3); 92.5 ($OC_{quart.}$); 119.0; 124.2; 125.2; 125.4; 126.3; 129.0; 129.1; 129.5; 134.0; 149.6; 151.0 (C═$C_{aromat.}$, C═N); 164.2 (C═O); MS (%): m/e = $M^{+\cdot}$ not found; 209 ([M-$C_6H_5NCSCH_3$]$^{+\cdot}$, 16); 150 ([$C_6H_5NCSCH_3$]$^{+\cdot}$, 100); 135 ([C_6H_5NCS]$^{+\cdot}$, 14); 77 ([C_6H_5]$^+$, 14). $C_{22}H_{17}NO_2S$ (359.4) requires C, 73.52; H, 4.77; N, 3.90; S, 8.92. Found C, 73.55; H, 4.79; N, 3.81; S, 9.09%.

4-Hydroxy-3-methylthio-2-phenyl-2H-isoquinolin-1-one 6a

Potassium *tert.* butoxide (2.24 g, 20 mmol) was added to a solution of phthalide **1** (R═H, sublimated, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78 °C with stirring. After the addition, the mixture was stirred for 2 h and iodo methane (2.84 g, 20 mmol) was added. Stirring of the resulting solution was continued for 2 h and then it was warmed up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The oily crude product separated was treated with ether to give a solid material which was recrystallized once from ethanol and acetone. Yield: 0.6 g (21.1%); m.p.: 173–86 °C; IR: 3410 (νOH, broad), 1635 (νC═O), 1590, 1560, 1530, 1480, 1450, 1325, 1250, 1200, 1150, 1090, 1020, 965, 890,

770, 750, 690, 660; ^{1}H-NMR (200 MHz; $CDCl_3$): 2.01 (s, 3H, SCH_3); 6.39 (s, 1H, OH, disappears with D_2O); 7.21–8.46 (m, 9H, aromat.); ^{13}C-NMR (50 MHz; $CDCl_3$): 19.3 (SCH_3); 116.1; 120.1; 122.4; 127.2; 128.5; 128.9; 129.0; 129.3; 130.1; 139.3; 140.4 (C═C, C═$C_{aromat.}$); 161.1 (C═O); MS (%): m/e = 283 (M^+, 67); 268 ($[M-CH_3]^+$, 48); 236 ($[M-SCH_3]^+$, 100); 133 ($[C_6H_4COCOH]^{+\cdot}$, 56); 104 ($[C_6H_4CO]^+$; 37); 77 ($[C_6H_5]^+$, 41); 76 ($[C_6H_4]^+$, 18). $C_{16}H_{13}NO_2S$ (283.3) requires C, 67.82; H, 4.62; N, 4.94; S, 11.32. Found C, 67.53; H, 4.65; N, 4.98; S 11.40%.

4-Hydroxy-3-(2-oxo-2-phenyl-ethylthio)-2-phenyl-2H-isoquinolin-1-one 6b

Potassium *tert.* butoxide (2.24 g, 20 mmol) was added with stirring to a solution of phthalide **1** (R═H, sublimated, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78°C. After the addition, the mixture was stirred for 2 h and ω-bromo acetophenone (1.99 g, 10 mmol) was added. Stirring of the resulting solution was continued for 2 h and then it was warmed up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The oily crude product solidified was recrystallized from ethanol. Yield: 1.4 g (36.1%); m.p.: 235–45°C (decomp.); IR: 3365 (νOH, broad), 1735 (νC═O_{ketone}), 1630 (νC═O_{amide}), 1615, 1590, 1460, 1370, 1280, 1200, 1170, 1100, 1080, 1060, 1040, 1010, 970, 900, 880, 850, 800, 780, 750, 730, 720, 690; ^{1}H-NMR (200 MHz; DMSO-d_6): 3.63 (d, 1H, SCH_2, ^2J = 11.81 Hz); 4.61(d, ^2J = 11.83 Hz; 1H, SCH_2); 6.81 (s, 1H, OH, disappears with D_2O); 6.98–8.04 (m, 14H, aromat.); ^{13}C-NMR (50 MHz; DMSO-d_6): 41.8 (SCH_2); 80.9; 94.5; 119.6; 124.3; 125.2; 126.8; 127.3; 127.5; 128.3; 129.4; 130.1; 134.1; 138.0; 145.6; 150.3 (C═C, C═$C_{aromat.}$); 167.6 (C═O); 171.0 (C═O); MS (%): m/e = 387 ($M^{+\cdot}$, 30); 235 ($[M-C_6H_5COCH_2SH]^{+\cdot}$, 85); 132 ($[C_6H_5COCO]^{+\cdot}$, 35); 105 ($[C_6H_5CO]^{+\cdot}$, 100); 104 ($[C_6H_4CO]^{+\cdot}$, 83); 77 ($[C_6H_5]^+$, 46); 76 ($[C_6H_4]^+$, 24). $C_{23}H_{17}NO_3S$ (387.5) requires C, 71.30; H, 4.42; N, 3.61; S, 8.28. Found C, 70.33; H, 4.33; N, 3.59; S, 8.26%.

3-[2-(4-Bromo-phenyl)-2-oxo-ethylthio]-4-hydroxy-2-phenyl-2H-isoquinolin-1-one 6c

Potassium *tert.* butoxide (2.24 g, 20 mmol) was added with stirring to a solution of phthalide **1** (R═H, sublimated, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78°C. After the addition, the mixture was stirred for 2 h and *p*-bromophenacyl bromide (2.78 g, 10 mmol) was added. Stirring of the resulting solution was continued for 2 h and then it was warmed

up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The precipitate was collected by filtration and recrystallized from ethanol. Yield: 1.57 g (34%); m.p.: 244–249°C; IR: ν = 3380 (νOH, broad), 1726 (νC=O$_{ketone}$), 1626 (νC=O$_{amide}$); ^{1}H-NMR (200 MHz; DMSO-d$_6$): 3.52(d, 1H, SCH$_2$, ^{2}J = 11.93 Hz); 4.47(d, ^{2}J = 12.0 Hz; 1H, SCH$_2$); 6.85 (s, 1H, OH); 6.87–8.0(m, 13H, aromat.); ^{13}C-NMR (50 MHz; DMSO-d$_6$): 41.4 (SCH$_2$); 80.6; 94.2; 119.5; 124.3; 125.2; 126.8; 127.3; 127.5; 128.3; 129.4; 129.5; 130.3; 130.5; 134.3; 137.4; 138.2; 145.3; 150.1 (C=C, C=C$_{aromat.}$); 167.5 (C=O); 170.7 (C=O); MS (%): m/e = 467 (M$^+$, 34); 232 (11); 268 (6); 235 (100); 183 (23); 171 (7); 147 (39); 132 (29); 104 (62); 76 (21). $C_{23}H_{16}BrNO_3S$ (466.36).

4-Hydroxy-3-[2-(4-nitro-phenyl)-2-oxo-ethylthio]-2-phenyl-2H-isoquinolin-1-one 6d

Potassium *tert.* butoxide (2.24 g, 20 mmol) was added with stirring to a solution of phthalide **1** (R=H, sublimated, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78°C. After the addition, the mixture was stirred for 2 h and *p*-nitrophenacyl bromide (2.44 g, 10 mmol) was added. Stirring of the resulting solution was continued for 2 h and then it was warmed up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The precipitate was collected by filtration and recrystallized from ethanol. Yield: 0.56 g (13%); m.p.: 250–5°C; ^{1}H-NMR (200 MHz; DMSO-d$_6$): 3.62 (d, 1H, SCH$_2$, ^{2}J = 12.08 Hz); 4.60 (d, ^{2}J = 12.09 Hz; 1H, SCH$_2$); 6.90 (s, 1H, OH); 6.94–8.09 (m, 13H, aromat); ^{13}C-NMR (50 MHz; DMSO-d$_6$): 41.4 (SCH$_2$); 80.6; 94.3; 119.5; 122.5; 124.5; 125.3; 126.4; 127.1; 128.8; 129.4; 130.4; 134.5; 145.0; 145.5; 147.3; 150.0 (C=C, C=C$_{aromat}$); 170.3 (C=O); MS (%): m/e = 432 (M$^{+\cdot}$, 24); 402 (1); 297 (4); 280 (5); 268 (6); 235 (100); 151 (11); 147 (31); 132 (16); 104 (46); 76 (19). $C_{23}H_{16}N_2O_5S$ (432.45).

3-(3,3-Dimethyl-2-oxo-butylthio)-4-hydroxy-2-phenyl-2H-isoquinolin-1-one 6e

Potassium *tert.* butoxide (2.24 g, 20 mmol) was added with stirring to a solution of phthalide **1** (R=H, sublimated, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78°C. After the addition, the mixture was stirred for 2 h and 1-bromo-3,3-dimethylbutan-2-one (1.79 g, 10 mmol) was added. Stirring of the resulting solution was continued for 2 h and then it was

warmed up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The precipitate was collected by filtration and recrystallized from ethanol. Yield: 0.76 g (21%); m.p.: 242–4°C; ^{1}H-NMR (200 MHz; DMSO-d_6): 0.75 (s, 9H, $C(CH_3)_3$); 3.40 (d, 1H, SCH_2, ^2J = 12.04 Hz); 3.95 (d, ^2J = 12.04 Hz; 1H, SCH_2); 6.00 (s, 1H, OH); 6.75–7.94 (m, 9H, aromat.); ^{13}C-NMR (50 MHz; DMSO-d_6): 27.0 ($C(CH_3)_3$); 40.8 (SCH_2); 83.3; 95.2; 119.3; 124.7; 124.9; 126.4; 127.6; 129.2; 130.0; 134.3; 148.7; 150.2 (C═C, C═$C_{aromat.}$); 168.3 (C═O); 173.5 (C═O); MS (%): m/e = 367 ($M^{+\cdot}$, 100); 268 (4); 235 (89); 176 (42); 165 (16); 147 (100); 129 (16); 104 (39); 86 (72); 77(15); 57 (29). $C_{21}H_{21}NO_3S$ (367.46).

3-Oxo-N,N-diphenyl-3H-isobenzofuran-1,1-dicarboximidothioic acid dimethyl ester 7

Potassium *tert.* butoxide (1.12 g, 10 mmol) was added with stirring to a solution of phthalide **1** (R═H, 1.34 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in dry THF (30 ml) at −78°C. After the addition, the mixture was stirred for 1.5 h and chlorotrimethylsilane (1.08 g, 10 mmol) was added. After 1.5 h stirring the second equivalent potassium *tert.* butoxide was added (1.12 g; 10 mmol). Then stirring was continued for 1.5 h and methyl iodide (1.42 g, 10 mmol) was added dropwise to the mixture. Stirring of the resulting solution was continued for 2 h and then it was warmed up to room temperature and further stirred. After several hours the mixture was poured onto ice (400 g). The precipitate was collected by filtration and recrystallized from acetonitrile. Yield: 0.45 g (20.8%); m.p.: 162–3°C; IR: 1785 (νC═O), 1625, 1600, 1585, 1460, 1370, 1310, 1280, 1250, 1200, 1180, 1150, 1110, 1090, 1050, 990, 960, 900, 880, 850, 765, 735, 700; ^{1}H-NMR (200 MHz; $CDCl_3$): 2.07 (s, 6H, 2 SCH_3); 6.81–7.98 (m, 14H, aromat.); ^{13}C-NMR (20 MHz; $CDCl_3$): 15.9 (SCH_3); 93.6; 119.2; 124.3; 125.4; 126.6; 129.9; 130.3; 133.9; 147.6; 148.3 (C═$C_{aromat.}$); 161.6 (C═N); 169.0 (C═O); MS (%): m/e = $M^{+\cdot}$ not found; 387 ([M- ·SCH_3 + H·]$^+$, 5); 150 ([$C_6H_5NCSCH_3$]$^{+\cdot}$, 100); 135 ([C_6H_5NCS]$^{+\cdot}$, 16); 104 ([C_6H_4CO]$^{+\cdot}$, 9); 77 ([C_6H_5]$^+$, 13). $C_{24}H_{20}N_2O_2S_2$ (432.6) requires C, 66.62; H, 4.66; N, 6.48; S, 14.82. Found C, 66.42; H, 4.63; N, 6.38; S, 14.98%.

X-ray Crystallography

A summary of crystal data along with details of the structure determination is given in table III. All measurements were performed on a Stoe STADI4 diffractometer using graphite-monochromated MoKα radiation in the ω-Θ scanning

TABLE III Summary of crystal data and experimental details for compounds **3a**, **6a** and **7**

	3a	*6a*	*7*
Empirical formula	$C_{15}H_{11}NO_2S$	$C_{16}H_{13}NO_2S$	$C_{24}H_{20}N_2O_2S_2$
Molecular weight [g mol^{-1}]	269.31	283.33	432.54
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Lattice parameters			
a [Å]	9.047(3)	13.6227(10)	10.419(3)
b [Å]	9.184(3)	7.3527(6)	10.882(3)
c [Å]	9.566(3)	13.7397(12)	11.564(3)
α [°]	70.539(11)	90.0	68.889(12)
β [°]	63.441(10)	97.271	64.013(13)
γ [°]	73.154(11)	90.0	75.962(12)
V [Å^3]	660.9(4)	1365.2(2)	1093.8(6)
Z	2	4	2
F(000)	280	592	452
D_{calc} [g cm^{-3}]	1.353	1.379	1.313
μ (MoK_α) [cm^{-1}]	0.241	0.237	0.266
crystal dimensions [mm]	0.19 × 0.30 × 0.51	0.10 × 0.15 × 0.46	0.30 × 0.30 × 0.34
Check reflections	($\bar{4}00$), (020), (002)	(200), (020), (002)	($\bar{3}00$), (152), (003)
Intensity variation [%]	3.8	7.1	6.8
$2\theta_{max.}$ [°]	60.0	60.0	56.0
hkl range	±12, ±12, ±13	±19, ±10, ±19	±13, ±14, ±15
Measured reflections	7682	7941	10575
Unique reflections	3842	3976	5288
R_{int}	0.0193	0.1149	0.0542
Weighting coefficients a/b*)	0.0445/0.1428	0.0466/0.0279	0.0353/0.0000
R1/wR2/S ($I > 2\sigma(I)$)	0.0359/0.0920/1.100	0.0577/0.0780/1.162	0.0457/0.0876/1.152
R1/wR2/S (all data)	0.0563/0.1015/1.024	0.2262/0.1117/0.997	0.1223/0.1070/0.919
$(\Delta/\rho)_{max}$ in last l.s. cycle	0.000	0.000	0.000
$\Delta\rho_{fin}$ (min./max.) [e Å^{-3}]	−0.387/0.306	−0.236/0.190	−0.267/0.246

*)$w = \frac{1}{[\sigma^2(F_0^2) + (a(\cdot)P)^2 + b(\cdot)P]}$ where $P = \frac{1}{3}(F_0^2 + 2F_c^2)$

mode at room temperature. Lattice constants were obtained by a least-squares treatment of the setting angles of 80 reflections in a Θ-range of 10.0–15.9 (**3a**), 10.3–18.7 (**6a**) and 10.1–18.7° (**7**), respectively. Lorentz and polarization corrections were applied during data reduction, absorption effects were neglected. All three structures were solved by direct methods (program system SHELXS-86[39]). Structure refinement on F^2 was performed using the full-matrix least-squares techniques of SHELXL-93.[40] The H atom positions for **3a** were found in a difference Fourier map and refined isotropically, those for **6a** and **7** were determined by geometric calculations and not refined. Final non-H atomic parameters are summarized in tables IV to VI. The molecular structures in figure 2 were plotted by use of the program XP/PC.[41]

TABLE IV Atomic coordinates and equivalent displacement parameters for **3a**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atoms	*x/a*	*y/b*	*z/c*	U_{eq}	*Atoms*	*x/a*	*y/b*	*z/c*	U_{eq}
S1	0.24410(6)	0.55453(4)	0.57148(4)	0.0527(2)	C7	0.1681(2)	0.5115(2)	0.1194(2)	0.0530(7)
O1	0.5360(1)	0.7596(1)	0.1363(1)	0.0463(4)	C8	0.2136(2)	0.6076(2)	−0.0349(2)	0.0531(7)
O2	0.5886(2)	0.8887(1)	−0.1208(1)	0.0642(6)	C9	0.3247(2)	0.7076(2)	−0.0872(2)	0.0484(6)
N1	0.3070(2)	0.8447(1)	0.4027(1)	0.0399(5)	C10	0.2178(2)	0.9260(2)	0.5286(2)	0.0392(5)
C1	0.3254(2)	0.6934(2)	0.4123(1)	0.0369(5)	C11	0.0663(2)	0.8925(2)	0.6514(2)	0.0486(6)
C2	0.4369(2)	0.6421(2)	0.2563(1)	0.0378(5)	C12	−0.0117(2)	0.9763(2)	0.7701(2)	0.0615(8)
C3	0.5123(2)	0.7977(2)	−0.0041(2)	0.0435(5)	C13	0.0585(3)	1.0920(2)	0.7656(2)	0.0689(9)
C4	0.3887(2)	0.7086(1)	0.0199(1)	0.0377(5)	C14	0.2064(3)	1.1282(2)	0.6407(3)	0.070(1)
C5	0.3425(2)	0.6141(1)	0.1744(1)	0.0350(5)	C15	0.2871(2)	1.0456(2)	0.5208(2)	0.0540(7)
C6	0.2304(2)	0.5136(2)	0.2272(2)	0.0447(6)					

TABLE V Atomic coordinates and equivalent displacement parameters for **6a**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atoms	*x/a*	*y/b*	*z/c*	U_{eq}	*Atoms*	*x/a*	*y/b*	*z/c*	U_{eq}
S1	0.84513(5)	0.2049(1)	0.92097(5)	0.0467(2)	C7	0.5006(2)	−0.0834(4)	1.1621(2)	0.050(1)
O1	0.7040(2)	−0.4204(3)	0.9429(2)	0.0632(8)	C8	0.5648(2)	0.0412(4)	1.1307(2)	0.044(1)
O2	0.6933(1)	0.2852(3)	1.0606(1)	0.0507(7)	C9	0.6328(2)	−0.0146(4)	1.0674(2)	0.036(1)
N1	0.7608(1)	−0.1299(3)	0.9363(1)	0.0379(8)	C10	0.7815(2)	0.2734(4)	0.8038(2)	0.059(1)
C1	0.6993(2)	0.1118(4)	1.0283(2)	0.038(1)	C11	0.8291(2)	−0.1966(4)	0.8711(2)	0.039(1)
C2	0.7611(2)	0.0549(4)	0.9655(2)	0.036(1)	C12	0.8002(2)	−0.2072(4)	0.7724(2)	0.051(1)
C3	0.7004(2)	−0.2599(4)	0.9700(2)	0.044(1)	C13	0.8656(2)	−0.2762(4)	0.7121(2)	0.061(1)
C4	0.6338(2)	−0.1955(4)	1.0388(2)	0.037(1)	C14	0.9572(2)	−0.3330(4)	0.7506(2)	0.062(1)
C5	0.5687(2)	−0.3206(4)	1.0736(2)	0.044(1)	C15	0.9851(2)	−0.3230(5)	0.8494(3)	0.066(1)
C6	0.5016(2)	−0.2645(4)	1.1335(2)	0.049(1)	C16	0.9215(2)	−0.2542(4)	0.9102(2)	0.055(1)

TABLE VI Atomic coordinates and equivalent displacement parameters for **7**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atoms	*x/a*	*y/b*	*z/c*	U_{eq}	*Atoms*	*x/a*	*y/b*	*z/c*	U_{eq}
S1	0.43526(8)	0.96436(6)	−0.16359(8)	0.0695(4)	C10	0.6263(2)	0.8002(2)	−0.3345(2)	0.043(1)
S2	0.04344(6)	0.74744(6)	0.18647(6)	0.0496(3)	C11	0.6375(3)	0.8579(2)	−0.4660(2)	0.052(1)
O1	0.1502(2)	0.8402(1)	−0.0973(1)	0.0426(7)	C12	0.7626(3)	0.9085(3)	−0.5645(2)	0.058(1)
O2	−0.0156(2)	0.8378(2)	−0.1707(2)	0.0635(10)	C13	0.8787(3)	0.8998(3)	−0.5341(3)	0.058(1)
N1	0.4969(2)	0.7455(2)	−0.2352(2)	0.0458(9)	C14	0.8697(3)	0.8402(3)	−0.4050(3)	0.061(1)
N2	0.3369(2)	0.6941(2)	0.1214(2)	0.0415(9)	C15	0.7440(3)	0.7899(3)	−0.3042(2)	0.056(1)
C1	0.2628(2)	0.7496(2)	−0.0601(2)	0.036(1)	C16	0.2723(3)	1.0342(2)	−0.0558(3)	0.068(1)
C2	0.0814(2)	0.7792(2)	−0.1377(2)	0.045(1)	C17	0.2300(2)	0.7276(2)	0.0882(2)	0.036(1)
C3	0.1484(2)	0.6428(2)	−0.1273(2)	0.040(1)	C18	0.3272(2)	0.6807(2)	0.2518(2)	0.042(1)
C4	0.1167(3)	0.5433(2)	−0.1560(2)	0.051(1)	C19	0.3010(3)	0.7918(2)	0.2925(3)	0.054(1)
C5	0.1951(3)	0.4218(2)	−0.1341(3)	0.057(1)	C20	0.3021(3)	0.7793(3)	0.4157(3)	0.069(2)
C6	0.2996(3)	0.4002(2)	−0.0841(3)	0.054(1)	C21	0.3271(3)	0.6577(4)	0.4976(3)	0.073(2)
C7	0.3300(2)	0.4994(2)	−0.0548(2)	0.046(1)	C22	0.3532(3)	0.5469(3)	0.4571(3)	0.066(1)
C8	0.2535(2)	0.6219(2)	−0.0791(2)	0.036(1)	C23	0.3567(2)	0.5570(2)	0.3332(3)	0.054(1)
C9	0.4047(2)	0.8091(2)	−0.1563(2)	0.038(1)	C24	0.0198(3)	0.6225(3)	0.3449(3)	0.063(1)

Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404551 (**3a**), CSD-404553 (**6a**) and CSD-404552 (**7**), respectively, the names of the authors, and the journal citation.

Acknowledgement

The authors thank the Fonds der chemischen Industrie for support. Thanks are due to Mademoiselle Rozenn Morin (E.N.S.C.R, Rennes, France) for her experimental work during practical trainee course.

References

[1] W. Dölling and T. Gildenast, *Phosphorus, Sulfur, and Silicon*, **82**, 163 (1993).
[2] F. W. Heinemann, W. Dölling, T. Gildenast, and H. Hartung, *J. Chem. Crystallography*, **25**, 237 (1995).
[3] Y. Ogawa, K. Hosaka, M. Chin, and Mitsuhashi, *Heterocycles*, **32**, 1737 (1991).
[4] J. L. Bloomer, and M. E. Lankin, *Tetrahedron Lett.*, **33**, 2769 (1992).
[5] E. Napolitano, G. Spinelli, R. Fiaschi, and A. Marsili, *Synthesis*, 38 (1985).
[6] D. W. Knight, and G. Pattenden, *J. Chem. Soc. Perkin Trans. I*, 635 (1975).
[7] R. K. Howe, *J. Org. Chem.*, **38**, 4164 (1973).
[8] M. Watanabe, S. Ijichi, H. Morimoto, K. Nogami, and S. Furukawa, *Heterocycles*, **36**, 553 (1993).
[9] P. G. Sammes, and D. J. Dodsworth, *J. Chem. Soc. Chem. Commun.*, 1979, 33.
[10] R. L. Horton, and K. C. Murdock, *J. Org. Chem.*, **25**, 938 (1960).
[11] G. A. Kraus, and H. Sugimoto, *Tetrahedron Lett.*, 2263 (1978).
[12] A. Beňo, P. Hrnčiar, and M. Lácová, *Collect. Czech. Chem. Commun.*, **37**, 3295 (1972).
[13] P. Hrnčiar, *Chem. Zvesti*, **14**, 96 (1962).
[14] H. Zimmer, and R. D. Barry, *J. Org. Chem.*, **27**, 1602 (1962).
[15] H. D. Becker, *J. Org. Chem.*, **29**, 3070 (1964).
[16] W. Trueb, and C. H. Eugster, *Helv. Chim. Acta*, **55**, 969 (1972).
[17] A. Bräm, and C. H. Eugster, *Helv. Chim. Acta*, **5**, 974 (1972).
[18] J. D. Dodsworth, M.-P. Calagno, E. U. Ehrmann, A. M. Quesada, O. Nunez, and P. G. Sammes, *J. Chem. Soc. Perkin Trans. I*, 1453 (1983).
[19] M. Iwao, H. Inoue, and T. Kuraishi, *Chem. Lett.*, 1263 (1984).
[20] A. S. Mitchell, and R. A. Russell, *Tetrahedron*, **51**, 5207 (1995).
[21] A. K. Mukerjee, and R. Ashare, *Chem. Rev.*, **91**, 1 (1991).
[22] R. Carceller, J. L. Garcia-Navio, M. L. Izquierdo, J. Alvares-Builla, J. Sanz-Aparicio, and F. Florencio, *Heterocycles*, **29**, 1877 (1989).
[23] G. V. Tormoz, V. Yu. Khordorkovski, and O. Neilands, *Khim. Geterotsikl. Soedin.*, 1989, 276.
[24] C. Alvares-Irarra, M. Gil, P. Ortiz, and M. Quiroga, *Heterocycles*, **27**, 2177 (1988).
[25] S. Masson, V. Mothes, and A. Thuillier, *Tetrahedron*, **40**, 1573 (1984).
[26] A. Shafiee, and G. Fanaii, *Synthesis*, 510 (1984).
[27] W.-D. Rudorf, and R. Schwarz, *Z. Chem.*, **28**, 58 (1988).
[28] M. Augustin, and W. Dölling, *J. Prakt. Chem.*, **324**, 322 (1982).
[29] M. Augustin, and W. Dölling, *Z. Chem.*, **30**, 395 (1990).
[30] H. Junjappa, H. Ila, and C. V. Asokan, *Tetrahedron*, **46**, 5423 (1990).
[31] S. Gabriel, and J. Colman, *Ber. Dtsch. Chem. Ges.*, **33**, 980 (1900).
[32] A. E. Walter, A. E. Baue, S. P. Walter, and R. B. Kampare, *Latv. PSR. Zinat Akad. Vestis, Kim. Ser.*, 111 (1983).

[33] J. Ozols, E. Liepinsch, B. Mazeika, B. Vigante, and G. Dubur, *Latv. PSR. Zinat Akad. Vestis, Kim. Ser.*, 583 (1978).
[34] Sara Pascual, Marie Christine Escudier, Anne Marie Lamazouere, Jean Sotiropoulos, L. Dupont, O. Dideberg, and G. Germain, *Phosphorus, Sulfur, Silicon, and Relat. Elem.*, **78**, 97 (1993).
[35] P. Rademacher, "*Strukturen organischer Moleküle*", VCH, Weinheim (1987).
[36] M. Jaskolski, "*Proceedings of the 4th Symposium on Organic Crystal Chemistry*", Poznań-Kierz, pp. 221–243 (1982).
[37] H. Simonis, E. Marben, and E. Mermold, *Ber. Dtsch. Chem. Ges.*, **38**, 3981 (1905).
[38] E. Mermold, and H. Simonis, *Ber. Dtsch. Chem. Ges.*, **41**, 982 (1908).
[39] G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, Universität, Göttingen (1986).
[40] G. M. Sheldrick, *SHELXS-93, Program for the Refinement of Crystal Structures*, Universität, Göttingen (1993).
[41] *XP/PC, Molecular Graphics Program Package for Display and Analysis of Stereochemical Data, Version 4.2 for MS-DOS*, Siemens Analytical X-Ray Instruments, Inc., Madison, Wisconsin, USA (1990).