N(2)—N(1)—C(4)—C(3)	10.6 (2)
N(1)—C(4)—C(3)—C(2)	−12.6 (2)
N(1)—N(2)—C(2)—C(3)	−6.0 (2)
Phenyl rings	
C(3)—C(4)—C(11)—C(12)	−72.0 (3)
C(3)—C(4)—·C(11) C(16)	103.1 (2)
C(5)—C(17)—C(18)—C(23)	−155.5 (2)
C(5)—C(17)—C(18)—C(19)	21.7 (4)

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed by full-matrix least-squares methods. Non-H atoms were refined anisotropically. All H atoms were found from difference maps, atoms H(1)–H(11) and H(15) (total of 12 atoms) were refined with fixed isotropic displacement parameters (1.2 × B_{eq} of the parent atom), but the other H atoms were not refined.

Data collection: Rigaku *AFC-5S* software (Rigaku Corporation, 1988). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1989). Data reduction: *TEXSAN*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *WINDOWS* 3.1.

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1-Benzoyl-3-(4-methoxyphenyl)thiourea

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Abstract

In the title molecule, $C_{15}H_{14}N_2O_2S$, there is an intramolecular N—H···O hydrogen bond of 2.618 (4) Å between an amide N atom and the benzoyl O atom, which completes a nearly planar six-membered ring in the central part of the molecule. The benzene rings of the benzoyl and methoxyphenyl groups make dihedral angles of 28.8 (4) and 44.2 (4)°, respectively, with this plane. In the crystal, the molecules are packed in a centrosymmetric manner through weak N—H···S interactions.

Comment

During our systematic search for non-linear optical organic crystals having short cut-off wavelengths, we isolated the title compound, 1-benzoyl-3-(4-methoxyphenyl)thiourea, (I).

(I)
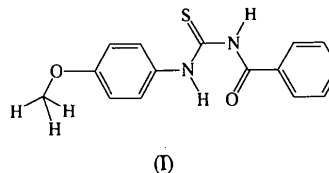
Since we have no access to the Cambridge Structural Database (Allen *et al.*, 1979), a search of Chemical Abstracts was carried out on compounds of type R–C_6H_4–CO–NH–CS–NH–C_6H_4–R'. One similar determination, with R = Cl and R' = H, was found (Simonov, Pobedimskaya, Martin & Masia, 1988), and there are no significant geometrical differences between that and the present determination. An intramolecular hydrogen bond [N1—H7···O1 2.618 (4) Å] completes an almost planar six-membered ring with the C1, N2 and C8 atoms; the maximum deviation from the best plane through the five non-H atoms is 0.014 (6) Å and the distance of the S atom from this plane is 0.0905 (2) Å. Weak intermolecular interactions were also found; N2—H13···S^i 3.507 (3), C7—H5···S^i 3.363 (3), C15—H1···$O1^{ii}$ 3.387 (6) and C11—H12···$O1^{iii}$ 3.424 (4) Å [symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $1-x$, $1-y$, $-z$; (iii) $1-x$, $1-y$, $1-z$]. All these interactions play a role in the centrosymmetric packing. From the last

two hydrogen-bonding distances, weak intermolecular hydrogen bonding between the benzoyl O atom and H—C_{sp^2} could be assumed (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Krishnamohan Sharma & Desiraju, 1994).
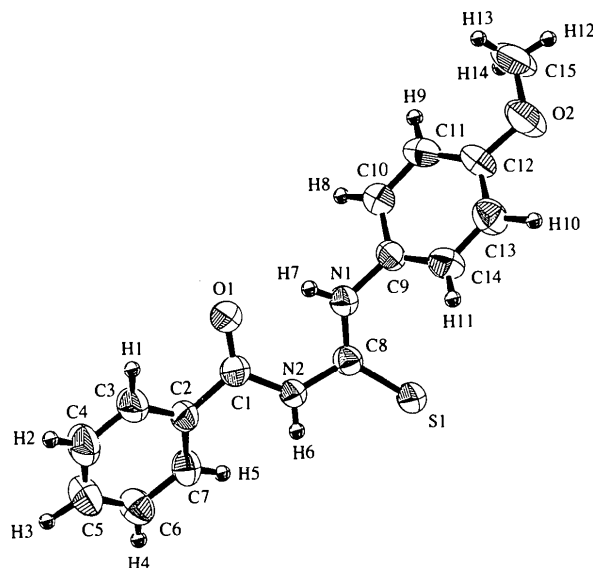

Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.

Experimental

The synthesis of the title compound was carried out by adding 6 ml benzoyl chloride to a solution of 6 g KSCN in 50 ml dry acetone. After removal of the residue, the filtrate was added to a solution of 6 g p-methoxyaniline in 50 ml dry acetone and the resulting solution stirred at 333 K for 2 h. Recrystallization was carried out three times from acetone.

Crystal data

$C_{15}H_{14}N_2O_2S$	Mo $K\alpha$ radiation
$M_r = 286.35$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 9.835\,(1)$ Å	$\theta = 23.26–26.56°$
$b = 13.484\,(1)$ Å	$\mu = 0.228$ mm^{-1}
$c = 5.440\,(1)$ Å	$T = 293$ K
$\alpha = 93.51\,(1)°$	Prismatic
$\beta = 93.68\,(1)°$	$0.30 \times 0.20 \times 0.20$ mm
$\gamma = 91.462\,(10)°$	Colorless
$V = 718.3\,(2)$ Å^3	
$Z = 2$	
$D_x = 1.324$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7R diffractom-	$R_{int} = 0.010$
eter	$\theta_{max} = 22.50°$
$\omega–2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction:	$k = -14 \rightarrow 14$
none	$l = -5 \rightarrow 5$
1751 measured reflections	3 standard reflections
1622 independent reflections	monitored every 200
1261 observed reflections	reflections
[$I > 3\sigma(I)$]	intensity decay: 0.19%

Refinement

Refinement on F	Weighting scheme based
$R = 0.0330$	on measured e.s.d.'s;
$wR = 0.0480$	$w = 1/[\sigma^2(F)]$
$S = 1.510$	$(\Delta/\sigma)_{max} = 0.029$
1261 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
234 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H-atom parameters added	Extinction correction: none
theoretically and refined	Atomic scattering factors
isotropically	from *International Tables*
	for X-ray Crystallography
	(1974, Vol. IV)

Table 1. *Fractional atomic 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	0.3664 (2)	0.0982 (2)	0.3330 (2)	0.0623
O1	0.7228 (2)	0.2996 (2)	0.6307 (4)	0.0743
O2	0.1447 (3)	0.4653 (2)	−0.2896 (4)	0.0851
N1	0.5032 (3)	0.2709 (2)	0.3339 (5)	0.0542
N2	0.5946 (2)	0.1559 (2)	0.5878 (4)	0.0455
C1	0.7021 (3)	0.2145 (2)	0.6926 (5)	0.0511
C2	0.7925 (3)	0.1710 (2)	0.8818 (5)	0.0473
C3	0.9271 (4)	0.2050 (3)	0.9101 (7)	0.0630
C4	1.0145 (4)	0.1690 (3)	1.0887 (7)	0.0746
C5	0.9695 (4)	0.0989 (3)	1.2396 (7)	0.0715
C6	0.8367 (4)	0.0651 (3)	1.2119 (6)	0.0634
C7	0.7475 (4)	0.1003 (2)	1.0339 (5)	0.0523
C8	0.4921 (3)	0.1803 (2)	0.4153 (5)	0.0448
C9	0.4094 (3)	0.3186 (2)	0.1725 (5)	0.0484
C10	0.3759 (4)	0.4149 (2)	0.2388 (7)	0.0648
C11	0.2886 (4)	0.4668 (3)	0.0880 (7)	0.0694
C12	0.2340 (3)	0.4220 (2)	−0.1300 (5)	0.0585
C13	0.2688 (4)	0.3258 (2)	−0.1984 (6)	0.0628
C14	0.3559 (4)	0.2747 (3)	−0.0477 (6)	0.0577
C15	0.1114 (6)	0.5667 (3)	−0.2290 (1)	0.0945

Table 2. *Selected geometric parameters (Å, °)*

S1—C8	1.659 (3)	C3—C4	1.374 (5)
O1—C1	1.231 (4)	C4—C5	1.374 (5)
O2—C12	1.363 (4)	C5—C6	1.365 (5)
O2—C15	1.438 (5)	C6—C7	1.380 (5)
N1—C8	1.329 (4)	C9—C10	1.381 (4)
N1—C9	1.425 (4)	C9—C14	1.370 (4)
N2—C1	1.376 (4)	C10—C11	1.383 (5)
N2—C8	1.392 (4)	C11—C12	1.367 (5)
C1—C2	1.476 (4)	C12—C13	1.386 (4)
C2—C3	1.386 (4)	C13—C14	1.375 (4)
C2—C7	1.383 (4)		
C12—O2—C15	117.1 (3)	S1—C8—N1	125.4 (2)
C8—N1—C9	127.9 (3)	S1—C8—N2	119.2 (2)
C1—N2—C8	128.7 (3)	N1—C8—N2	115.4 (3)
O1—C1—N2	121.5 (3)	N1—C9—C10	117.8 (3)
O1—C1—C2	121.2 (3)	N1—C9—C14	123.1 (3)
N2—C1—C2	117.3 (3)	O2—C12—C11	124.6 (3)
C1—C2—C3	117.9 (3)	O2—C12—C13	115.8 (3)
C1—C2—C7	122.8 (3)		

The structure of (I) was solved by direct methods (SAPI91; Fan, 1991) and expanded using Fourier techniques (Beurskens et al., 1992). The weighting scheme was based on counting statistics and included a factor $P = 0.03$ to downweight the intense reflections. *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement and *TEXSAN* (Molecular Structure Corporation, 1992) was used for data reduction, structure refinement and the preparation of material for publication.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bandrowski's Base

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Abstract

Molecules of N,N''-(2,5-diamino-2,5-cyclohexadiene-1,4-diylidene)bis(1,4-benzenediamine), $C_{18}H_{18}N_6$, lie across crystallographic inversion centres. The angle between

the central ring and each of the terminal rings is 60.2 (5)°. Hydrogen bonding links molecules into chains along **b**.

Comment

Although first prepared over a century ago (Bandrowski, 1889) the title compound, (1), has been little studied. It is generally prepared by oxidation of 1,4-phenylenediamine with either $K_3[Fe(CN)_6]$ (Bandrowski, 1889; Bandrowski, 1894; Ritter & Schmitz, 1929) or H_2O_2 (*e.g.* Corbett, 1972; Rice, 1962), although nitrobenzene has also been used as the oxidizing agent (Crippa, Bellani & Marubini, 1930). It has also been observed as a product of ceruloplasmin oxidation of 1,4-phenylenediamine under *in vitro* enzymic conditions (Rice, 1962; Fan & Wang, 1984). We obtained a crystalline sample of (1) as a side product (see below) of an attempt to produce 1,4-bis(2-cyanoguanidinyl)benzene following the method described for the preparation of N-aryl-2-cyanoguanidines (Cunningham, Wan & Cox, 1994). The molecular structure of (1) was determined from early chemical studies (Green, 1913; Ritter & Schmitz, 1929; Lauer & Sunde, 1939; Sunde & Lauer, 1952) and from a determination of its formation mechanism (from 1,4-phenylenediamine *via* condensation of a quinonediimine intermediate; Corbett, 1972). Little is known of its chemistry; treatment with either acid or base results in decomposition to 1,4-phenylenediamine (Cox & Lewin, 1935; Feigl & Costa Neto, 1956).

(1)

(2)
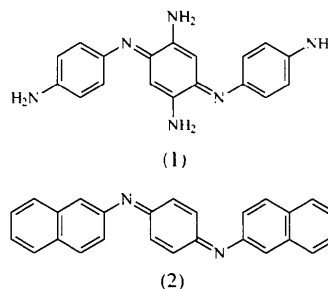
Molecules of (1) lie across crystallographic inversion centres (Fig. 1) and the central ring is therefore ideally planar. The angle between central and terminal rings is 60.2 (5)° and the two terminal rings are coplanar by symmetry. Comparison with the published structure of N,N'-(2,5-cyclohexadiene-1,4-diylidene)bis(2-naphthalenamine), (2) (Povet'eva, Chetkina & Kopilov, 1980) shows general similarities in the central N,N'-(2,5-cyclohexadiene-1,4-diylidene) moiety: the C=N double bonds are almost identical in length [1.298 (6) Å in (1) and 1.293 and 1.296 Å for the two independent half-molecules in (2)]. The C=C double bond length of 1.361 (7) Å in (1) is longer than in (2) where values of 1.322 and 1.326 Å are found; we attribute both this and the greater disparity between the C—C single bond lengths in (1) [1.432 (7) and 1.485 (6) Å] to the