Crystal structure of benzoyl(4-chlorophenylhydrazono)methyl phenyl sulfone, $C_{20}H_{15}ClN_2O_3S$, and benzoyl(4-bromophenylhydrazono)methyl phenyl sulfone, $C_{20}H_{15}BrN_2O_3S$, *two isomorphous β-ketosulfones*

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Abstract

$C_{20}H_{15}ClN_2O_3S$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.227(3)$ Å, $b = 18.949(4)$ Å, $c = 9.156(2)$ Å, $\beta = 107.34(2)°$, $V = 1859.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.079$, $wR_{ref}(F^2) = 0.231$, $T = 293$ K.

$C_{20}H_{15}BrN_2O_3S$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.412(2)$ Å, $b = 18.994(3)$ Å, $c = 9.100(2)$ Å, $\beta = 107.85(2)°$, $V = 1877.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.062$, $wR_{ref}(F^2) = 0.220$, $T = 293$ K.

Source of material

The title compounds were synthesized by the reaction of benzoylmethyl phenyl sulfone with 4-chlorophenyldiazonium chloride and 4-bromophenyldiazonium chloride, respectively [1]. Crystals used for data collection were obtained by vapour diffusion: the chloride and bromide samples were dissolved in a 2:1 mixture of chloroform and isopropyl alcohol and equilibrated at room temperature against pure isopropyl alcohol for 6 and 8 days, respectively.

Experimental details

The bromide compound shows high rate of crystal decomposition, 42% within 50 h of X-ray data collection. The full data set was collected using two crystals. Both individual data sets were scaled on common reflections and merged together with SHELXTL-plus [2].

Discussion

Present work is part of a project aimed at structural studies of modified β-ketosulfones [3-5]. In this paper, the structures of two isomorphous benzoyl(4-chlorophenylhydrazono)methyl phenyl sulfone **1** and benzoyl(4-bromophenylhydrazono)methyl phenyl sulfone **2** from the X-ray data are reported. The superposition of both structures **1** and **2** shows very high similarity of their conformations. The root-mean-square deviation computed from the least-squares fit of all relevant non-H atoms (Cl and Br atoms were excluded from the calculations) is only 0.08 Å. In both independent molecules, one of the sulfonyl double bonds (S=O2), the β-carbonyl group and the phenylhydrazone moiety are approximately coplanar. Their configuration may be defined as EZE. These three letters indicate, relatively to the C=N bond, positions of the carbonyl C=O and sulfonyl S=O double bond as well as the N—C bond bearing the phenyl ring [5,6]. Structures **1** and **2** are stabilized by strong resonance assisted intramolecular hydrogen bonds [7]) linking the hydrazone moieties and sulfonyl groups. The resulting cyclic six-membered rings are practically planar. The root-mean-square deviations from the ring plane are 0.02 Å for both structures. The intramolecular N2···O2 distances [2.680(5) Å and 2.673(7) Å, respectively] are much shorter than the sum of respective van der Waals radii, 3.07 Å [8]. Electrostatic attraction of the oppositely charged atoms generates short intramolecular contacts beetwen the S···O3 and O1···C2 pairs of atoms [2.923(3) Å, 3.203(5) Å and 2.934(5) Å, 3.197(8) Å for **1** and **2**, respectively]. Bond lengths distibutions in **1** and **2** are similar to those observed in related compounds [3-5]. In particular, the S1—C1 and S2—C23 bonds are longer [1.793(6) Å and 1.783(6) Å, respectively] than the conventional S—C(sp^2) single bond, 1.751 Å [9].

1. Benzoyl(4-chlorophenylhydrazono)methyl phenyl sulfone, $C_{20}H_{15}ClN_2O_3S$

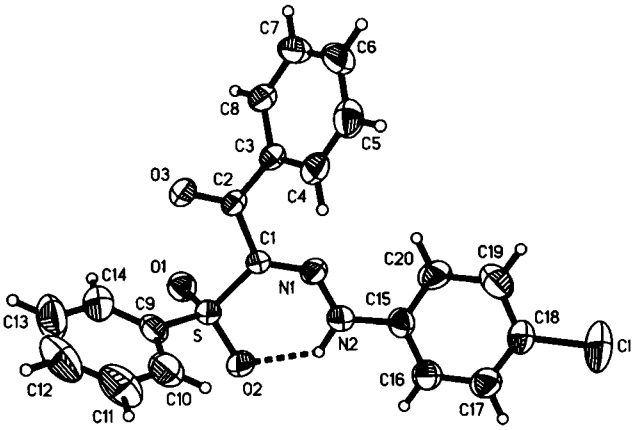

Table 1. Data collection and handling.

Crystal:	intensive-yellow prism, size 0.15 × 0.40 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.41 cm^{-1}
Diffractometer, scan mode:	Siemens P3, $\omega/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3944, 3200
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2432
$N(param)_{refined}$:	249
Programs:	SHELXTL-plus [2], SHELXS-97 [10], SHELXL [11]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	1.001(4)	0.292(2)	0.284(2)	0.079(8)
H(4)	4*e*	1.0652	0.1086	0.0457	0.052(6)
H(5)	4*e*	1.2015	0.0448	–0.0469	0.052
H(6)	4*e*	1.2917	–0.0566	0.0711	0.052
H(7)	4*e*	1.2475	–0.0958	0.2869	0.052
H(8)	4*e*	1.1103	–0.0341	0.3829	0.052
H(10)	4*e*	0.7168	0.2335	0.065	0.079(8)
H(11)	4*e*	0.5357	0.1958	–0.114	0.079

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12)	4*e*	0.421	0.1067	–0.0485	0.079
H(13)	4*e*	0.4881	0.0524	0.1808	0.079
H(14)	4*e*	0.672	0.0883	0.3622	0.079
H(16)	4*e*	1.089	0.3908	0.2049	0.079
H(17)	4*e*	1.2337	0.4479	0.1188	0.079
H(19)	4*e*	1.3967	0.2633	0.0828	0.079
H(20)	4*e*	1.2505	0.2064	0.1794	0.079

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	4*e*	0.85125(9)	0.19232(5)	0.3599(1)	0.0386(6)	0.0328(6)	0.0529(6)	0.0021(4)	0.0179(4)	0.0005(4)
Cl	4*e*	1.4376(2)	0.4059(1)	0.0269(3)	0.085(1)	0.122(2)	0.160(2)	–0.029(1)	0.068(1)	0.029(1)
O(1)	4*e*	0.8576(3)	0.1650(2)	0.5066(3)	0.048(2)	0.052(2)	0.054(2)	0.001(1)	0.018(1)	–0.003(1)
O(2)	4*e*	0.8590(3)	0.2680(2)	0.3450(4)	0.059(2)	0.030(2)	0.095(2)	0.004(1)	0.041(2)	0.001(2)
O(3)	4*e*	0.9112(3)	0.0434(2)	0.3373(4)	0.054(2)	0.034(2)	0.078(2)	–0.003(1)	0.035(2)	0.004(1)
N(1)	4*e*	1.0576(3)	0.1943(2)	0.2569(4)	0.036(2)	0.034(2)	0.049(2)	–0.003(1)	0.007(2)	0.005(1)
N(2)	4*e*	1.0632(3)	0.2617(2)	0.2512(5)	0.042(2)	0.035(2)	0.071(2)	0.002(2)	0.022(2)	0.001(2)
C(1)	4*e*	0.9741(3)	0.1572(2)	0.2946(4)	0.033(2)	0.028(2)	0.050(2)	0.002(2)	0.014(2)	0.004(2)
C(2)	4*e*	0.9823(4)	0.0788(2)	0.2891(4)	0.037(2)	0.028(2)	0.046(2)	–0.004(2)	0.011(2)	0.003(2)
C(3)	4*e*	1.0753(4)	0.0446(2)	0.2255(5)	0.038(2)	0.026(2)	0.051(2)	–0.005(2)	0.013(2)	–0.005(2)
C(4)	4*e*	1.1018(4)	0.0676(2)	0.0953(5)	0.049(2)	0.036(2)	0.058(2)	–0.010(2)	0.018(2)	–0.003(2)
C(5)	4*e*	1.1830(5)	0.0292(2)	0.0402(6)	0.061(3)	0.057(3)	0.062(3)	–0.014(2)	0.033(2)	–0.012(2)
C(6)	4*e*	1.2371(5)	–0.0314(3)	0.1103(7)	0.052(3)	0.052(3)	0.094(4)	0.002(2)	0.035(3)	–0.017(3)
C(7)	4*e*	1.2105(4)	–0.0547(2)	0.2386(6)	0.048(2)	0.041(2)	0.079(3)	0.008(2)	0.016(2)	–0.004(2)
C(8)	4*e*	1.1292(4)	–0.0177(2)	0.2966(5)	0.044(2)	0.033(2)	0.053(2)	–0.002(2)	0.013(2)	0.001(2)
C(9)	4*e*	0.7119(4)	0.1638(2)	0.2282(5)	0.032(2)	0.050(2)	0.052(2)	0.007(2)	0.014(2)	0.001(2)
C(10)	4*e*	0.6710(5)	0.1965(3)	0.0881(6)	0.049(3)	0.075(3)	0.062(3)	0.012(2)	0.018(2)	0.012(2)
C(11)	4*e*	0.5629(5)	0.1748(4)	–0.0179(7)	0.054(3)	0.120(5)	0.064(3)	0.020(3)	0.003(3)	0.004(3)
C(12)	4*e*	0.4955(6)	0.1211(4)	0.0214(8)	0.044(3)	0.120(6)	0.084(4)	0.010(3)	0.003(3)	–0.029(4)
C(13)	4*e*	0.5349(5)	0.0890(4)	0.1583(8)	0.046(3)	0.095(5)	0.107(5)	–0.021(3)	0.017(3)	–0.015(4)
C(14)	4*e*	0.6449(5)	0.1100(3)	0.2668(6)	0.051(3)	0.064(3)	0.073(3)	–0.005(2)	0.019(2)	0.005(2)
C(15)	4*e*	1.1558(4)	0.2940(2)	0.1981(5)	0.036(2)	0.043(2)	0.050(2)	–0.005(2)	0.011(2)	–0.003(2)
C(16)	4*e*	1.1513(4)	0.3651(2)	0.1809(5)	0.041(2)	0.045(2)	0.063(3)	–0.003(2)	0.010(2)	0.000(2)
C(17)	4*e*	1.2370(4)	0.3991(2)	0.1291(5)	0.048(2)	0.042(2)	0.063(3)	–0.004(2)	0.009(2)	0.002(2)
C(18)	4*e*	1.3281(4)	0.3618(3)	0.0921(6)	0.044(2)	0.051(3)	0.069(3)	–0.011(2)	0.020(2)	0.004(2)
C(19)	4*e*	1.3352(5)	0.2889(3)	0.1085(6)	0.048(3)	0.070(3)	0.081(4)	0.006(2)	0.025(3)	–0.011(3)
C(20)	4*e*	1.2470(4)	0.2550(2)	0.1648(6)	0.055(3)	0.031(2)	0.079(3)	–0.005(2)	0.013(2)	–0.004(2)

2. Benzoyl(4-bromophenylhydrazono)methyl phenyl sulfone, $C_{20}H_{15}BrN_2O_3S$

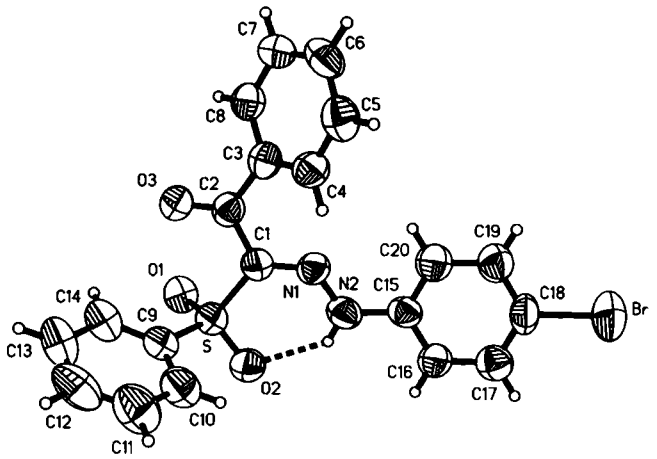

Table 4. Data collection and handling.

Crystal:	yellow prism, size 0.25 × 0.30 × 0.35 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	42.26 cm^{-1}
Diffractometer, scan mode:	KUMA Diffraction KM-4, $\omega/2\theta$
$2\theta_{max}$:	130°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3017, 3017
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1503
$N(param)_{refined}$:	248
Programs:	SHELXTL-plus [2], SHELXS-97 [10], SHELXL [11]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.489(5)	0.284(2)	-0.277(3)	0.09(1)
H(4)	4e	0.4349	0.1073	-0.0428	0.063(8)
H(5)	4e	0.3011	0.0442	0.0474	0.063
H(6)	4e	0.2057	-0.0554	-0.0797	0.063
H(7)	4e	0.2573	-0.0975	-0.2908	0.063
H(8)	4e	0.3938	-0.0354	-0.3816	0.063
H(10)	4e	0.7868	0.2389	-0.0634	0.14(2)
H(11)	4e	0.9693	0.1999	0.1172	0.14
H(12)	4e	1.0753	0.1092	0.0640	0.14
H(13)	4e	1.0087	0.0500	-0.1685	0.14
H(14)	4e	0.8215	0.0834	-0.3503	0.14
H(16)	4e	0.4118	0.3898	-0.2055	0.09
H(17)	4e	0.2686	0.4474	-0.1159	0.09
H(19)	4e	0.1147	0.2596	-0.0760	0.09
H(20)	4e	0.2576	0.2046	-0.1752	0.09

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	4e	0.6493(2)	0.19136(9)	-0.3552(2)	0.059(1)	0.0600(9)	0.069(1)	-0.0013(8)	0.0216(8)	0.0002(8)
Br	4e	0.0599(1)	0.40526(7)	-0.0174(2)	0.0958(8)	0.132(1)	0.163(1)	0.0192(6)	0.0630(8)	-0.0310(8)
O(1)	4e	0.6437(4)	0.1638(2)	-0.5029(5)	0.071(3)	0.080(3)	0.059(3)	0.003(2)	0.022(2)	0.007(2)
O(2)	4e	0.6409(5)	0.2657(2)	-0.3421(6)	0.080(3)	0.061(3)	0.094(3)	-0.009(3)	0.040(3)	-0.002(3)
O(3)	4e	0.5897(5)	0.0422(2)	-0.3331(6)	0.074(3)	0.058(3)	0.106(4)	0.001(2)	0.042(3)	-0.003(3)
N(1)	4e	0.4460(5)	0.1917(3)	-0.2528(6)	0.057(3)	0.050(3)	0.067(3)	0.004(3)	0.012(3)	0.001(3)
N(2)	4e	0.4405(5)	0.2601(3)	-0.2491(6)	0.060(3)	0.063(4)	0.074(4)	-0.007(3)	0.024(3)	0.007(3)
C(1)	4e	0.5286(6)	0.1546(3)	-0.2891(7)	0.058(4)	0.056(4)	0.063(4)	-0.001(3)	0.019(3)	0.001(3)
C(2)	4e	0.5209(6)	0.0777(3)	-0.2862(7)	0.057(4)	0.059(4)	0.059(4)	0.004(3)	0.012(3)	-0.002(3)
C(3)	4e	0.4263(6)	0.0436(3)	-0.2249(7)	0.060(4)	0.060(4)	0.054(4)	0.010(3)	0.013(3)	0.005(3)
C(4)	4e	0.3988(7)	0.0666(4)	-0.0936(8)	0.065(4)	0.055(4)	0.076(5)	0.004(3)	0.019(4)	0.009(3)
C(5)	4e	0.3188(7)	0.0290(4)	-0.0407(9)	0.073(5)	0.099(6)	0.073(5)	0.005(4)	0.028(4)	-0.004(4)
C(6)	4e	0.2629(7)	-0.0315(4)	-0.1152(9)	0.060(4)	0.089(6)	0.095(6)	-0.001(4)	0.033(4)	0.026(5)
C(7)	4e	0.2923(7)	-0.0561(4)	-0.2423(9)	0.068(5)	0.065(4)	0.086(5)	-0.012(3)	0.028(4)	-0.006(4)
C(8)	4e	0.3736(6)	-0.0188(4)	-0.2963(8)	0.064(4)	0.065(4)	0.064(4)	0.007(3)	0.018(3)	0.003(3)
C(9)	4e	0.7894(6)	0.1631(4)	-0.2203(8)	0.056(4)	0.067(4)	0.068(4)	-0.008(3)	0.019(3)	-0.001(3)
C(10)	4e	0.8300(7)	0.2005(5)	-0.0835(9)	0.070(5)	0.102(6)	0.074(5)	-0.008(4)	0.024(4)	-0.008(4)
C(11)	4e	0.9396(9)	0.1772(6)	0.023(1)	0.083(6)	0.145(9)	0.079(6)	-0.006(6)	0.020(5)	-0.003(6)
C(12)	4e	1.0025(9)	0.1231(6)	-0.009(1)	0.060(5)	0.152(9)	0.077(6)	-0.018(6)	0.003(4)	0.007(6)
C(13)	4e	0.9625(8)	0.0870(6)	-0.148(1)	0.062(5)	0.130(8)	0.116(7)	0.017(5)	0.027(5)	0.007(6)
C(14)	4e	0.8519(7)	0.1070(4)	-0.257(1)	0.059(5)	0.102(6)	0.083(5)	0.002(4)	0.022(4)	0.004(5)
C(15)	4e	0.3489(6)	0.2925(3)	-0.1962(8)	0.050(4)	0.056(4)	0.068(4)	-0.002(3)	0.010(3)	0.005(3)
C(16)	4e	0.3515(7)	0.3640(4)	-0.1799(8)	0.059(4)	0.056(4)	0.080(5)	0.005(3)	0.015(4)	0.001(3)
C(17)	4e	0.2669(7)	0.3987(4)	-0.1266(8)	0.063(4)	0.073(5)	0.071(4)	0.001(4)	0.011(4)	0.001(4)
C(18)	4e	0.1785(7)	0.3583(4)	-0.0893(9)	0.063(4)	0.084(5)	0.081(5)	0.017(4)	0.030(4)	-0.011(4)
C(19)	4e	0.1736(7)	0.2857(4)	-0.1036(9)	0.067(5)	0.078(5)	0.081(5)	0.005(4)	0.022(4)	-0.004(4)
C(20)	4e	0.2600(7)	0.2531(4)	-0.1609(9)	0.068(5)	0.068(5)	0.092(5)	0.006(4)	0.020(4)	0.002(4)

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