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Predominance of Amino-Sulfonyl Hydrogen Bonding in (*Z*)-2-Benzene-sulfonyl-1-phenyl-2-(phenylhydrazono)ethanones in Crystals and in Solution: An Experimental NMR and X-ray Crystallographic and Theoretical *Ab Initio* and DFT/GIAO Studies

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^{1}H, ^{13}C, and ^{15}N NMR spectra show that (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanone is the only tautomeric form detected in chloroform solution. Substituent in the phenylhydrazone moiety does not affect this tautomeric preference. *Ab initio* calculations show that (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanone is really favoured over its proton transfer products in chloroform solution. This shows that N-H...OS(O) interaction is much stronger than the hydrogen bonds in other tautomeric forms. The (*Z*)-2-benzene-sulfonyl-1-phenyl-2-(phenylhydrazono)ethanone tautomer was also detected in the crystal state.

Key words: tautomers, monohydrazones of diketosulfones, hydrogen bonding, X-ray diffraction, NMR, DFT and *ab initio* calculations

2-Phenylhydrazone of 1,3-diphenyl-1,2,3-trione is the only tautomeric form detected in chloroform solution [1]. Substituent in the phenylhydrazone moiety does not affect this tautomeric preference. *Ab initio* calculations show that ketohydrazone tautomer is really very much favoured over its proton transfer products in chloroform solution [1]. Ketohydrazone was also the only tautomer detected in the crystal state [1]. Tautomeric preferences in related (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones, PhCOC(=NNHPh)SO_2Ph, were not studied earlier.

There is a great need for NMR information on sulfur because of the importance of this element in chemistry and biochemistry [2,3]. A special type of "double" bond between sulfur and oxygen atoms [4,5] is responsible for weak conjugation of S=O with other double bonds. On the other hand, owing to their strong inductive effect, alkyl and aryl sulfone groups, RSO_2, are powerful electron acceptors [6]. X-ray diffraction [7,8] and photoelectron studies [7] and *ab initio* calculations [7] show that there are

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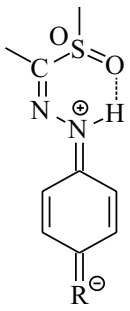
some interesting noncovalent interactions in β-ketosulfones that may affect transmission of the substituent effect in these compounds. Thus, the oxygen atoms of the SO_2 group points toward the oppositely charged carbonyl carbon atom, from which it is separated by a distance shorter than the sum of their van der Waals radii. Another through-space interaction of a similar type takes place between the carbonyl oxygen and sulfur atoms. The $O_{C=O}$–S distance is not as critically short as that between O_{SO_2} and $C_{C=O}$ [7]. Thus, a *gauche* conformation of the CH_2–S and carbonyl bonds (irrespective of aryl moieties and the gas or solid state) is a result of superposition of electronic interactions between ArCO and SO_2Ar groups and the non-bonding O→C and O→S interactions.

Stereoelectronic [9,10], rather than steric intramolecular interactions, were also found to affect the conformation of (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones [11]. Molecular conformation of these compounds is stabilized by strong resonance-assisted intramolecular hydrogen bonds, >N-H...O=S(O)< [11]. Electron-withdrawing substituents increase the positive charge on nitrogen and strengthen the hydrogen bond [11] (Scheme 1).

Scheme 1



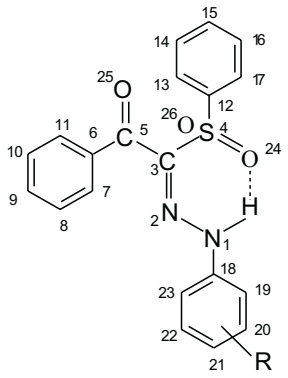
The negatively charged carbonyl oxygen atom in the molecule was found to be very close to the positively charged sulfur atom [11]. The $O_{C=O}$...S distance is less than the sum of their van der Waals radii. The O_{SO_2}...$C_{C=O}$ distance is also shorter than the sum of the oxygen and carbon radii [11]. These stereoelectronic interactions are most intense in compounds carrying strong electron-withdrawing substituents. Detailed analysis of the O...S and O...C non-bonding interactions show that the charge transfer from carbonyl towards sulfonyl groups is more efficient than that from SO_2 to CO [11].

^{1}H and ^{13}C [12] as well as ^{33}S [13] NMR spectra of substituted phenacylphenyl sulfones, R-C_6H_4-$COCH_2SO_2$-C_6H_4-R′, were earlier studied by us from point of view of the transmission of substituent effect. ^{1}H, ^{13}C and ^{15}N NMR spectra of substituted α-phenacyl-sulfonylacetanilides, R-C_6H_4-$NHCOCH_2SO_2$-Ph, were also recently discussed [14]. The results of the respective structural studies on (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones will be considered in the present paper.

EXPERIMENTAL

The compounds studied are these obtained earlier [15] by coupling of phenacylphenyl sulfone with substituted benzenediazonium chlorides [16]. After recrystallization from glacial acetic acid their mp's are as follows (°C): **1** (174–176), **2** (228–230), **3** (152–153), **4** (223–225), **5** (246–247), **6** (197–198), **7** (184–185), **8** (201–202), **9** (202–203), **10** (145–146), **11** (163–164), **12** (176–178), **13** (186–187), **14**

Scheme 2



	R		R
1	4-OMe	**11**	2-Br
2	4-Me	**12**	2,4-Cl_2
3	H	**13**	2,5-Cl_2
4	4-Cl	**14**	2,6-Cl_2
5	4-Br	**15**	3,4-Cl_2
6	3-Cl	**16**	3,5-Cl_2
7	3-Br	**17**	2,3,4-Cl_3
8	4-COPh	**18**	2,4,5-Cl_3
9	4-NO_2	**19**	2,4,6-Cl_3
10	2-Cl		

(126–127), **15** (208–209), **16** (230–231), **17** (199–200), **18** (147–148) and **19** (198–200). In general, the measured mp's (uncorrected) are the same (or higher) as these obtained earlier [15,16,18]. Satisfactory analytical data (± 0.3% for C, H, and N) were obtained for all compounds prepared.

^{1}H, ^{13}C and ^{15}N NMR experiments were run with a Bruker Avance DRX 500 spectrometer working at 500.13 MHz for proton, 125.77 MHz for carbon-13 and 50.69 MHz for nitrogen-15, respectively, and equipped with a 5 mm diameter inverse detection probehead and z-gradient accessory for 0.1–0.2 M solutions in $CDCl_3$ at 303 K. ^{1}H and ^{13}C NMR chemical shift assignments are based on homonuclear two-dimensional (2 D) double quantum filtered (DQF) COSY and (2 D) heteronuclear pulsed field gradient (PFG) selected ^{1}H, ^{13}C HMQC and HMBC experiments as described in our previous papers [19,20]. ^{1}H and ^{13}C NMR chemical shifts are referenced to the solvent signal 7.26 ppm from TMS in proton experiments and 77.00 ppm from TMS in carbon-13 experiments, respectively. ^{15}N NMR chemical shifts are measured from PFG ^{1}H, ^{15}N HMBC correlation maps produced by incorporating a 50 msec evolution time in the pulse sequence optimized for proton-nitrogen-15 spin-spin couplings of 10 Hz [19,20]. A 1 mm diameter capillary of CH_3NO_2 inserted coaxially inside the 5 mm diameter NMR-tube was used as an external reference for nitrogen-15 chemical shifts. Detailed NMR acquisition and processing parameters are available from E.K. on request.

The X-ray crystallographic data for both compounds were recorded with a Nonius Kappa CCD area-detector diffractometer using graphite monochromatised MoK_α radiation [$\lambda(MoK_\alpha)$ = 71.073 pm] and temperature of 173.0 ± 0.1 K for **3** and 150.0 ± 0.1 K for **12**, **14** and **17**. Lattice parameters were determined from 10 images recorded with 1° φ scans and subsequently refined on all data. The data collections

were performed using φ and ω scans with 5.0° steps for **3**, 1.0° steps for **12** and 2.0° steps for **14** and **17** and exposure times of 2× 20 s, 2× 10 s, 2×8 s and 2× 15 s per frame for **3**, **12**, **14** and **17**, respectively. The crystal-to-detector distance was fixed to 35 mm. The data were processed with Denzo-SMN v0.93.0 [21] and no absorption correction was applied.

The structures were solved by direct methods (SHELXS-97 [22]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97 [23]). The hydrogen atoms were located from the difference Fourier. An additional electron density peak in **12** was identified as 1/8 water, the hydrogens of which were not determined. Other experimental X-ray data are revealed in Table 1.

Table 1. Experimental data for the X-ray crystallographic studies on **3**, **12**, **14** and **17**.

	3	**12**	**14**	**17**
Formula	$C_{20}H_{16}N_2O_3S$	$C_{20}H_{14}Cl_2N_2O_3S \cdot 1/8H_2O$	$C_{20}H_{14}Cl_2N_2O_3S$	$C_{20}H_{13}Cl_3N_2O_3S$
Formula weight/g· mol^{-1}	364.41	435.37	433.29	467.73
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P –1 (No. 2)	C 2/c (No. 15)	P –1 (No. 2)	P –1 (No. 2)
Crystal size/mm	0.2×0.2×0.4	0.25×0.30×0.40	0.20×0.35×0.35	0.15×0.20×0.25
D_{calc}/Mg·m^3	1.420	1.523	1.530	1.500
a/Å	5.6299 (7)	22.8615 (6)	8.1923 (5)	7.6821 (5)
b/Å	11.286 (2)	8.1016 (2)	10.8954 (6)	10.3536 (6)
c/Å	14.042 (2)	20.7894 (5)	11.7019 (8)	13.654 (1)
α/°	102.356 (7)	90	67.813 (2)	100.366 (2)
β/°	97.161 (8)	99.623 (2)	76.533 (2)	101.495 (3)
γ/°	97.810 (8)	90	85.744 (2)	96.123 (2)
V/Å^3	852.5 (2)	3796.3 (2)	940.4 (1)	1035.4 (1)
Z	2	8	2	2
$\mu(MoK_\alpha)$/mm^{-1}	0.213	0.478	0.481	0.568
Reflections collected	4980	9997	5502	6069
Independent reflections	2958	3341	3272	3536
R_{int}	0.046	0.044	0.028	0.024
$\Delta\rho_{max}$, $\Delta\rho_{min}$/eÅ^{-3}	0.21, –0.37	0.22, –0.35	0.22, –0.37	0.21, –0.33
R, %[a]	4.86	3.57	3.98	3.67
R_w, %[a]	9.34	7.89	9.30	8.53
GOF	1.046	1.010	1.014	1.008

[a] $I > 2\sigma I$.

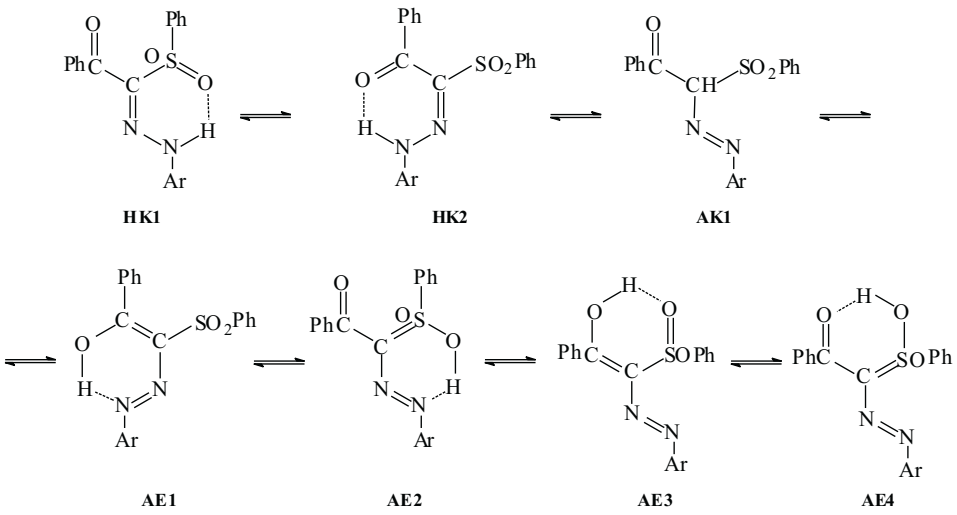
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 162313–162316. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. The substituent constants used are these compiled in ref. [24]. Quantum chemical calculations were performed at the HF and B3LYP levels of theory with the Gaussian 98 package [25]. Geometries were optimized to the global minima at the *ab initio* HF level with the 3-21G basis set using C1-symmetry (no symmetry constraints). The GIAO/DFT calculations for ^{13}C chemical shifts were performed at the B3LYP level with 6-311G basis set. The chemical shifts are referenced to TMS for ^1H and ^{13}C NMR (both in experiment and in calculations), and to nitromethane for ^{15}N NMR.

RESULTS AND DISCUSSION

Phenacylphenylsulfones, $PhCOCH_2SO_2Ph$, [3] can be easily transformed to (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones, $PhCOC(=NNHPh)SO_2Ph$ [15–17]. These compounds show antifungal activity [17]. Their molecules contain few different basic centres and thus, seem interesting from point of view of the tauto-

meric equilibria that can take place in their solutions (Scheme 3). Although the N-bound hydrogen atom may be attracted either by the carbonyl or sulfonyl oxygen atoms, the former type of hydrogen bond was believed to appear in the molecules of (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones [18]. This conclusion was based on the IR (nujol mulls and KBr pellets) and UV (solutions in various solvents) spectral data, which seem insufficient to distinguish unambiguously the >N-H...O=C< from >N-H...O=S(O)< hydrogen bond.

Scheme 3



The ^{1}H NMR chemical shift assignments of **1**–**19** are based on DQF ^{1}H, ^{1}H COSY [26,27] experiments, which distinguish unambiguously each aromatic spin system. These mutually separated spin systems have been further assigned based on PFG ^{1}H, ^{13}C HMQC [28,29] as well as PFG ^{1}H, ^{13}C HMBC and PFG ^{1}H, ^{15}N HMBC [30] experiments. The aromatic protons of the C=O bound phenyl ring showed clear PFG ^{1}H, ^{13}C HMBC cross-peaks to the carbonyl carbon, while the phenyl protons of the nitrogen bound ring were revealed from their PFG ^{1}H, ^{15}N HMBC cross peaks, respectively. The sulfur bound phenyl ring did not show any exocyclic long-range correlations in these HMBC experiments.

The chemical shift of H1 (Table 2) shows that this hydrogen atom is strongly attracted by the oxygen atom. It is not easy, however, to prove if it is carbonyl or sulfonyl oxygen atom. Even the ^{13}C NMR spectra show that the chemical shifts of two different carbonyl carbon atoms in 2-arylhydrazones of 1,3-diphenylpropane-1,2,3-

trione (only one of them is involved in the formation of the intramolecular hydrogen bond) are not very much different ($\Delta\delta < 2$ ppm [1]). The chemical shift of C5 for **1**–**19** is equal to *ca* 186 ppm (Table 3), which shows that the respective signal is upfield shifted as compared to that observed in the spectra of 2-arylhydrazones of 1,3-diphenyl-propane-1,2,3-trione [1]. It is noteworthy that GIAO/DFT calculated ^{13}C NMR chemical shifts are in agreement with the experimental ones, which are based on homonuclear DQF ^{1}H, ^{1}H COSY and heteronuclear PFG ^{1}H, ^{13}C HMQC and PFG ^{1}H, ^{13}C HMBC experiments (Tables 3 and 4). Higher basicity of the sulfonyl oxygen atom, as compared to that of carbonyl oxygen atom [31], suggests, however, that the N-bound hydrogen atom should be attracted stronger by the SO_2 than by CO group.

The chemical shifts of H1 show that these hydrogen atoms are acidic in all compounds studied. When *p*-NO_2 and *p*-COPh are excluded, the δ(H1) values are linearly dependent (substituent chemical shift, ΔSCS = 0.43 ppm) on σ and σ^+ substituent constants (correlation coefficients R = 0.962 and 0.918, respectively, for 9 correlation points). No simple dependences were found between δ(C3) and δ(C5) values and $\sigma^{(+)}$. Effect of the substituent on the chemical shift of C3 (ΔSCS = 5.09 ppm) is much more significant than that of C5 (ΔSCS = 0.29 ppm). Linear dependence on $\sigma^{(+)}$ was, however, observed for δ(N1) and δ(N2). Thus, $\delta(\mathrm{N1}) = -0.12\sigma - 26.45$ (correlation coefficient, R = 0.971 for 11 correlated points) and $\delta(\mathrm{N2}) = -0.16\sigma - 3.29$ (R = 0.984). It is noteworthy that similar correlations with the σ^+ constants are of much lower quality. The substituent chemical shift was found to be comparable for these two nitrogen atoms (ΔSCS = 16.8 and 17.4 ppm for N1 and N2, respectively). Dual-substituent parameter (DSP) analysis shows that for seven correlated points the resonance and field/inductive substituent effects are comparable to each other:

$$\delta(\mathrm{N1}) = -8.08\sigma_F - 6.60\sigma_R - 219.19 \quad (R = 0.984)$$
$$\delta(\mathrm{N2}) = -6.84\sigma_F - 7.03\sigma_R - 20.64 \quad (R = 0.994)$$

The chlorine atoms in both *ortho*, *i.e.* 19 and 23 positions cause a significant upfield effect of δ(N1) and significant downfield effect of δ(N2) (see Table 4).

The ^{13}C NMR chemical shifts were also calculated using the GIAO-HF/DFT level of theory. Parametrization used in these calculations for the carbon atoms attached to chlorine and bromine is insufficient to obtain reliable ^{13}C NMR chemical shifts (heavy atom effect). Quality of the δ_{calcd} *vs.* $\delta_{exp.}$ correlation (Table 3) is much better when these chemical shifts are excluded. Thus, the *ab initio* calculations at the HF/B3LYP level of theory (geometry optimization) with the 3-21G and 6-311G (GIAO calculations) basis sets reproduce the experimental ^{13}C chemical shifts with very good accuracy.

In general, both N1 and N2 signals in the ^{15}N NMR spectra of compounds **1**–**19** are upfield shifted (by *ca* 5 and 10 ppm, respectively) as compared to these in the ^{15}N NMR spectra of 2-arylhydrazones of 1,3-diphenylpropane-1,2,3-trione [1].

Table 2. Experimental ^{1}H NMR chemical shifts (δ) of compounds **1**–**19** for 0.1–0.2 M solutions in $CDCl_3$ at 303 K (vicinal coupling constants, in Hz, are given in parentheses).

	H1	H7(11)	H8(10)	H9	H13(17)	H14(16)	H15	H19	H20	H21	H22	H23
1[a]	12.46	8.16	7.63	7.59	7.76	7.54	7.52	7.12	7.90	–	7.90	7.12
		(7.8)	(7.5)	(7.5)	(7.8)	(8.2)	(7.2)	(9.0)	(7.3)		(7.3)	(9.0)
2[b]	12.43	8.17	7.58	7.66	7.78	7.41	7.52	7.16	7.08	–	7.08	7.16
		(7.2)	(7.1)	(7.4)	(6.9)	(7.7)	(6.8)	(8.2)	(8.5)		(8.5)	(8.2)
3	12.45	8.18	7.58	7.66	7.80	7.43	7.54	7.18	7.35	7.15	7.35	7.18
		(8.2)	(7.8)	(7.4)	(7.4)	(7.7)	(7.4)	(8.1)	(7.3)	(7.3)	(7.3)	(8.1)
4	12.39	8.16	7.59	7.67	7.77	7.54	7.42	7.32	7.01	–	7.01	7.32
		(8.3)	(7.8)	(6.9)	(7.1)	(7.4)	(7.7)	(8.5)	(8.5)		(8.5)	(8.5)
5	12.39	8.16	7.53	7.59	7.66	7.48	7.41	6.85	7.13	–	7.13	6.85
		(7.3)	(7.0)	(7.7)	(7.1)	(7.3)	(7.1)	(8.9)	(8.9)		(8.9)	(8.9)
6	12.34	8.15	7.57	7.66	7.77	7.53	7.26	7.18	–	7.42	7.03	7.03
		(7.7)	(7.8)	(7.4)	(7.6)	(7.7)	(8.1)	(8.0)		(7.8)	(8.0)	(8.1)
7	12.33	8.15	7.58	7.66	7.77	7.43	7.35	7.26	–	7.20	7.08	7.54
		(7.3)	(7.7)	(7.4)	(8.5)	(7.7)	(6.7)	(7.0)		(8.0)	(8.1)	(7.4)
8[c]	12.50	8.19	7.60	7.68	7.80	7.48	7.56	7.76	7.25	7.43	7.25	7.76
		(7.3)	(7.5)	(7.4)	(7.1)	(7.7)	(6.3)	(7.0)	(8.6)	(7.8)	(8.6)	(7.0)
9	12.49	8.24	8.17	7.69	7.79	7.62	7.58	7.25	7.45	–	7.45	7.25
		(9.1)	(7.3)	(7.4)	(7.1)	(8.1)	(5.4)	(8.9)	(7.8)		(7.7)	(8.9)
10	12.74	8.23	7.59	7.55	7.80	7.22	7.67	–	7.40	7.43	7.07	7.27
		(7.2)	(7.7)	(7.4)	(7.8)	(7.4)	(7.5)		(8.0)	(7.7)	(6.5)	(8.0)
11	12.71	8.24	7.59	7.68	7.81	7.59	7.52	–	7.43	7.01	7.43	7.25
		(7.3)	(7.2)	(7.5)	(7.1)	(7.6)	(5.4)		(7.9)	(7.1)	(7.9)	(6.3)
12	12.68	8.21	7.68	7.60	7.79	7.55	7.43	–	7.43	–	7.58	7.18
		(7.4)	(7.5)	(7.9)	(7.3)	(7.4)	(8.0)		(8.0)		(7.9)	(7.4)
13	12.64	8.20	7.69	7.60	7.81	7.58	7.57	–	7.57	7.45	–	7.02
		(7.3)	(7.4)	(8.0)	(7.8)	(6.1)	(6.0)		(6.0)	(7.7)		(8.6)
14	12.27	8.23	7.68	7.60	7.83	7.42	7.60	–	7.47	7.42	7.10	–
		(7.2)	(7.4)	(6.9)	(7.2)	(7.7)	(6.9)		(8.0)	(7.7)	(8.1)	
15	12.32	8.15	7.60	7.67	7.76	7.43	7.57	7.00	–	–	7.11	7.31
		(7.3)	(7.7)	(7.5)	(8.4)	(7.8)	(7.4)	(8.7)			(7.8)	(6.5)
16	12.28	8.15	7.60	7.69	7.77	7.45	7.56	7.06	–	7.11	–	7.06
		(7.3)	(7.8)	(7.4)	(7.1)	(7.7)	(7.4)	(7.0)		(7.8)		(7.0)

Table 2 (continuation)

17	12.71	8.21	7.66	7.69	7.79	7.43	7.57	–	–	–	7.12	7.31
		(7.3)	(7.8)	(7.5)	(7.1)	(7.8)	(7.7)				(9.0)	(9.0)
18	12.60	8.19	7.61	7.70	7.79	7.58	7.61	–	7.51	–	–	7.36
		(7.3)	(8.1)	(8.0)	(7.1)	(7.4)	(8.1)		(7.0)			(7.5)
19	12.21	8.21	7.61	7.69	7.79	7.48	7.48	–	7.33	–	7.33	–
		(7.3)	(7.7)	(6.6)	(7.2)	(7.5)	(7.5)		(7.5)		(7.5)	

[a]OC**H**$_3$: 3.79.
[b]CH_3: 2.34.
[c]CO**Ph**: *ortho* 6.79 (7.2), *meta* 6.66 (7.6), *para* 6.82 (7.5).

Table 3. Experimental and calculated (*italic*) ^{13}C (aromatic) NMR chemical shifts (δ) of compounds **1**–**19** for 0.1–0.2 M solutions in $CDCl_3$ at 303 K.

	C6	C7(11)	C8(10)	C9	C12	C13(17)	C14(16)	C15	C18	C19	C20	C21	C22	C23
1[a]	134.26	131.91	128.82	133.69	140.54	129.97	128.43	135.66	134.89	114.90	129.14	127.68	129.14	114.90
	137.43	*131.99*	*128.87*	*133.39*	*151.45*	*132.12*	*129.26*	*134.04*	*136.25*	*115.34*	*109.43*	*159.97*	*119.92*	*118.83*
		131.92	*129.07*			*125.66*	*127.80*							
2[b]	137.27	132.07	128.16	134.07	140.62	130.19	128.52	135.35	139.08	115.58	128.97	128.22	128.97	115.58
	137.32	*133.12*	*127.66*	*133.59*	*140.20*	*131.96*	*128.94*	*134.07*	*137.78*	*115.13*	*129.99*	*127.45*	*129.21*	*117.23*
		133.08	*127.30*			*125.60*	*127.63*							
3	137.04	130.07	128.47	132.16	141.19	129.65	128.41	134.12	140.37	115.53	128.95	127.77	128.95	115.53
	137.02	*132.96*	*127.46*	*133.74*	*151.25*	*131.90*	*129.22*	*134.23*	*142.16*	*117.29*	*130.00*	*126.06*	*130.39*	*114.65*
		132.01	*125.57*			*131.00*	*151.30*							
4	137.00	130.52	129.06	132.37	142.27	130.09	128.63	134.31	139.95	116.70	129.83	128.30	129.83	116.70
	136.98	*132.03*	*129.18*	*134.14*	*151.11*	*132.05*	*129.51*	*134.51*	*141.13*	*115.38*	*129.62*	*146.74*	*129.14*	*117.51*
		132.93	*127.50*			*125.77*	*128.05*							
5	134.33	132.38	128.82	132.60	140.42	130.09	128.63	132.75	136.97	117.03	129.07	128.31	129.07	117.03
	136.96	*132.03*	*129.24*	*134.07*	*150.96*	*131.88*	*129.47*	*134.56*	*141.14*	*114.94*	*133.24*	*138.25*	*132.79*	*117.20*
		132.16	*127.77*			*126.64*	*127.99*							
6	136.83	132.44	129.04	134.31	142.44	130.70	128.60	135.71	140.17	115.71	130.07	127.89	129.72	113.73
	136.36	*131.71*	*129.29*	*134.38*	*150.84*	*131.75*	*129.44*	*134.65*	*142.54*	*113.81*	*152.16*	*124.56*	*130.54*	*115.56*
		132.59	*128.08*			*125.40*	*127.89*							

Table 3 (continuation)

7	136.73	130.95	128.59	132.46	142.43	130.09	128.02	134.35	140.03	118.60	129.57	127.88	129.05	114.16
	136.49	*131.74*	*129.24*	*134.22*	*150.56*	*131.69*	*129.53*	*134.71*	*141.87*	*117.30*	*144.24*	*128.51*	*129.97*	*115.67*
		132.85	*127.58*			*125.59*	*127.84*							
8[c]	136.74	132.20	129.09	132.55	144.45	130.09	128.68	134.43	137.66	114.97	129.73	128.31	129.73	114.97
	136.91	*132.01*	*129.19*	*134.07*	*151.20*	*132.13*	*129.53*	*134.53*	*144.57*	*117.54*	*133.42*	*135.14*	*132.96*	*112.35*
		132.65				*125.19*	*127.87*							
9	139.61	134.70	129.20	136.42	146.12	132.91	130.07	136.43	144.21	115.25	131.95	128.79	131.95	115.25
	145.64	*134.86*	*128.15*	*136.67*	*150.70*	*132.69*	*129.52*	*135.03*	*146.65*	*115.74*	*131.95*	*126.26*	*129.81*	*113.33*
		132.73	*127.50*			*125.59*	*127.91*							
10	136.81	130.77	128.55	132.42	140.11	130.05	128.10	134.29	137.81	121.30	129.75	127.85	128.00	115.70
	135.12	*131.94*	*128.52*	*133.93*	*150.35*	*131.87*	*129.07*	*134.30*	*138.25*	*146.80*	*130.43*	*129.89*	*128.90*	*129.08*
		131.80	*127.79*			*126.37*	*128.12*							
11	136.86	132.47	128.90	132.97	140.17	130.71	128.75	134.34	139.01	116.11	129.06	128.32	130.13	110.69
	134.64	*132.03*	*128.57*	*134.04*	*150.54*	*131.60*	*128.88*	*134.01*	*141.28*	*140.93*	*134.17*	*130.06*	*128.80*	*130.06*
		131.79	*127.75*			*126.48*	*128.18*							
12	136.71	131.34	128.08	132.59	139.93	130.06	128.68	134.46	136.76	121.67	129.94	128.46	129.43	116.53
	134.87	*132.02*	*128.81*	*134.06*	*149.93*	*131.57*	*129.18*	*134.42*	*137.40*	*146.19*	*129.32*	*149.22*	*128.24*	*129.02*
		132.32	*127.75*			*126.45*	*127.91*							
13	136.54	132.78	129.13	134.24	139.85	131.74	128.72	134.53	138.77	119.32	130.69	127.99	130.12	115.95
	134.64	*132.09*	*128.74*	*134.28*	*149.97*	*131.78*	*129.05*	*134.48*	*138.31*	*145.27*	*130.48*	*128.80*	*148.85*	*127.99*
		132.52	*128.10*			*125.58*	*127.92*							
14	135.00	131.17	129.00	132.40	140.44	130.04	128.71	134.25	136.32	127.50	129.34	128.49	129.34	127.50
	135.01	*131.73*	*128.64*	*134.20*	*151.33*	*131.72*	*128.96*	*134.24*	*134.88*	*148.61*	*128.50*	*129.36*	*129.50*	*149.55*
		132.62	*128.13*			*125.40*	*127.91*							
15	134.46	131.33	128.69	132.56	140.01	130.19	128.52	133.69	136.74	117.26	130.07	128.39	129.11	114.74
	136.63	*131.86*	*129.35*	*134.59*	*150.90*	*132.04*	*129.65*	*134.63*	*141.22*	*115.34*	*147.06*	*141.17*	*142.89*	*115.66*
		131.60	*127.91*			*126.24*	*128.18*							
16	136.56	132.74	129.15	134.54	143.11	130.66	128.71	136.30	139.87	114.07	130.10	128.00	130.10	114.07
	136.49	*131.94*	*129.36*	*134.79*	*150.95*	*131.99*	*129.60*	*134.68*	*142.52*	*114.72*	*150.25*	*123.10*	*151.13*	*112.71*
		131.54	*127.76*				*128.25*							
17	134.59	132.33	129.07	132.74	139.79	132.09	128.98	134.59	138.17	121.06	130.07	128.74	129.15	113.91
	134.74	*131.93*	*128.87*	*134.27*	*149.74*	*131.49*	*129.21*	*134.48*	*138.44*	*126.88*	*128.53*	*146.58*	*142.89*	*144.45*
		131.86	*127.85*			*126.50*	*128.04*							

Table 3 (continuation)

18	136.47	129.18	129.55	132.90	139.71	128.80	128.40	132.15	130.80	117.09	130.11	137.45	128.04	134.65
	134.21	*132.10*	*128.81*	*134.50*	*149.87*	*131.65*	*129.18*	*134.61*	*136.96*	*128.62*	*144.41*	*144.60*	*130.15*	*144.05*
		131.78	*127.80*			*126.40*	*127.92*							
19	134.41	132.28	129.29	132.56	140.29	131.71	129.20	134.01	136.25	127.81	130.52	129.10	130.52	127.81
	134.51	*131.80*	*128.81*	*134.60*	*151.30*	*131.82*	*129.07*	*134.53*	*134.29*	*147.65*	*127.52*	*147.63*	*128.39*	*148.61*
		126.05	*127.86*			*132.14*	*128.61*							

[a]O**C**H$_3$: 55.51 (*51.89*).
[b]**C**H$_3$: 20.88 (*19.77*).
[c]**CO**Ph: carbonyl 195.09 (*196.49*), *ipso* 140.01 (*139.65*), *ortho* 133.93 (*132.00*, *133.93*), *meta* 129.73 (*127.26*, *129.93*), *para* 130.56 (*132.83*).

Table 4. Experimental ^{15}N and $^{13}C^{a}$ (non-aromatic) NMR chemical shifts (δ) of compounds **1**–**19** for 0.1–0.2 M solutions in $CDCl_3$ at 303 K.

	N1	N2	C3	C5
1	–218.1	–19.9	128.01	186.34
			124.81	*182.02*
2	–218.5	–19.8	127.45	186.42
			126.23	*182.31*
3	–219.2	–20.6	125.30	186.46
			125.54	*182.51*
4	–222.3	–22.3	127.90	186.38
			126.44	*182.86*
5	–222.4	–22.5	127.90	186.38
			126.30	*182.79*
6	–223.3	–23.0	125.09	186.31
			126.90	*182.91*
7	–223.3	–22.9	123.52	186.31
			126.61	*182.79*
8	–222.2[b]	–23.6	127.95	186.34
			126.91	*182.80*
9[b]	–225.2	–26.5	125.82	186.24
			126.12	*183.50*
10	–224.9	–25.7	125.26	186.32
			126.98	*180.51*
11	–221.2	–25.4	125.74	186.43
			126.85	*178.92*
12	–227.2	–27.6	127.94	186.29
			127.97	*180.33*
13	–227.8	–28.3	124.97	186.26
			128.05	*180.44*
14	–232.8	–12.5	127.71	186.50
			127.75	*181.05*
15	–225.1	–24.3	127.96	186.27
			127.45	*183.04*
16	–226.5	–25.5	124.81	186.23
			127.71	*183.25*
17	–227.0	–28.5	128.01	186.24
			128.31	*180.42*
18	–229.9	–29.9	128.10	186.21
			128.73	*180.28*
19	–234.9	–14.3	128.61	186.46
			128.64	*180.90*

[a]Calculated chemical shifts in *italic*. [b]$\delta(^{15}NO_2)$: –13.3 ppm.

Table 5. Selected bond lengths/interatomic distances (pm) and bond and dihedral angles (°) for compounds **3**, **12**, **14**, and **17**.

	3	**12**	**14**	**17**
N1–N2	130.8(3)	131.5(3)	130.7(3)	135.1(3)
N2–C3	131.2(3)	130.0(3)	130.6(3)	131.3(3)
C3–S4	178.1(3)	179.5(2)	179.0(2)	179.8(2)
C3–C5	148.2(3)	148.9(3)	148.4(3)	152.2(3)
C5–O25	122.5(3)	122.2(3)	122.2(3)	123.1(3)
S4–O24	145.3(2)	144.5(2)	145.0(2)	147.4(2)
S4–O26	143.5(2)	143.3(2)	143.1(2)	144.6(2)
S4–C12	176.5(3)	176.1(2)	175.8(3)	175.9(2)
O24...N1	267.0(3)	268.9(2)	264.5(3)	266.6(2)
S4...O25	297.6(2)	298.5(2)	295.1(2)	301.4(2)
C5...O24	394.0(3)	394.1(3)	393.6(3)	400.1(3)

Table 5 (continuation)

C5...O26	322.2(3)	315.2(3)	321.9(3)	311.0(3)
C18N1N2	120.0(2)	118.2(2)	119.5(3)	119.8(2)
N1N2C3	123.7(2)	125.4(2)	123.6(2)	125.3(2)
N2C3S4	126.3(2)	125.3(2)	125.8(2)	123.8(2)
N2C3C5	117.0(2)	116.0(2)	117.9(2)	118.8(2)
C3S4O24	106.2(1)	104.9(1)	105.7(1)	105.5(1)
C3S4O26	112.6(1)	110.3(1)	111.6(1)	109.3(1)
O26S4O24	117.4(1)	119.4(1)	117.2(1)	119.6(1)
O24S4C12	108.5(1)	108.3(1)	107.7(1)	107.6(1)
O26S4C12	108.8(1)	109.8(1)	110.0(1)	108.9(1)
C3S4C12	102.2(1)	102.7(1)	103.7(1)	104.9(1)
S4C12C13	119.5(2)	120.2(2)	119.6(2)	119.0(2)
C5C6C7	121.7(2)	122.7(2)	122.1(2)	122.7(2)
N2N1C18C19	173.2(2)	–168.3(2)	–100.2(3)	172.2(2)
C20C19C18N1	–178.0(2)	179.6(2)	–174.0(2)	–179.3(2)
C8C7C6C5	–169.6(2)	–174.7(2)	–172.6(2)	177.0(2)
C14C13C12S4	176.9(2)	174.2(2)	178.5(2)	179.2(2)
C18N1N2C3	–179.5(2)	176.3(2)	–179.8(2)	–178.4(2)
N1N2C3S4	2.2(3)	–2.3(3)	–2.2(4)	1.5(3)
N2C3S4O26	–127.6(2)	146.9(2)	–122.5(2)	–147.5(2)
N2C3S4O24	2.2(3)	17.1(2)	5.9(3)	–17.6(2)
N2C3C5O25	163.5(2)	155.5(2)	163.7(2)	–154.2(2)
O24S4C12C17	58.8(2)	–34.1(2)	56.4(2)	34.8(2)
O26S4C12C13	10.0(2)	17.7(2)	6.5(2)	–13.9(2)
C3C5C6C7	–52.3(3)	–38.7(3)	–43.3(3)	25.2(3)
C3C5C6C11	135.8(2)	145.0(2)	142.0(3)	–158.0(2)
O25C5C6C7	125.2(3)	143.9(2)	134.8(3)	–154.9(2)
S4C3C5O25	–17.0(3)	–13.8(3)	–14.3(3)	18.7(3)
C5C3S4O24	–177.3(2)	–174.6(2)	–176.3(2)	169.7(2)
C5C3S4O26	53.0(2)	–44.8(2)	55.3(2)	39.9(2)
C5C3S4C12	–63.6(2)	72.2(2)	–63.1(2)	–76.7(2)
C3S4C12C13	129.3(2)	–99.6(2)	126.0(2)	103.1(2)
C3S4C12C17	–53.1(2)	76.5(2)	–55.4(2)	–77.2(2)
S4C3C5C6	160.5(2)	168.7(2)	163.8(2)	–161.4(2)

The molecular geometry for **3**, **12**, **14** and **17** is shown in Fig. 1.

X-ray diffraction studies show that strong resonance-assisted intramolecular hydrogen bonds of the >N-H...O=S(O)< type takes place in the crystal (no >NH...O=C< was detected in any case). Significant twist of the S- and C-bound benzene rings with respect to the C3S4O24 and C3C5O25 planes can be seen. The benzoyl fragments are also twisted out of the N2C3S4O24 plane. Non-planarity of the N2C3C5O25 fragment causes that conjugation of the carbonyl and imine moieties is not very much effective. Two *ortho* chlorine atoms in the phenylhydrazone moiety cause a significant twisting of the *respective* benzene ring out of the C3N2N1C18 plane.

Analysis of the X-ray data in Table 5 shows that the S4...O25 and C5...O26 interatomic distances are very short, which confirms the presence of strong stereo-electronic interactions between $O_{C=O}$ and S, as well as O_{SO_2} and $C_{C=O}$ [11].

Ab initio calculations were shown recently [1] to predict correctly the preferred tautomer in solution. As it can be seen in Table 6, **HK1** is the most stable among different forms presented in Scheme 3. The NMR spectra (Tables 2–4) show that it is the only tautomeric form present in chloroform solution irrespective of the substituent

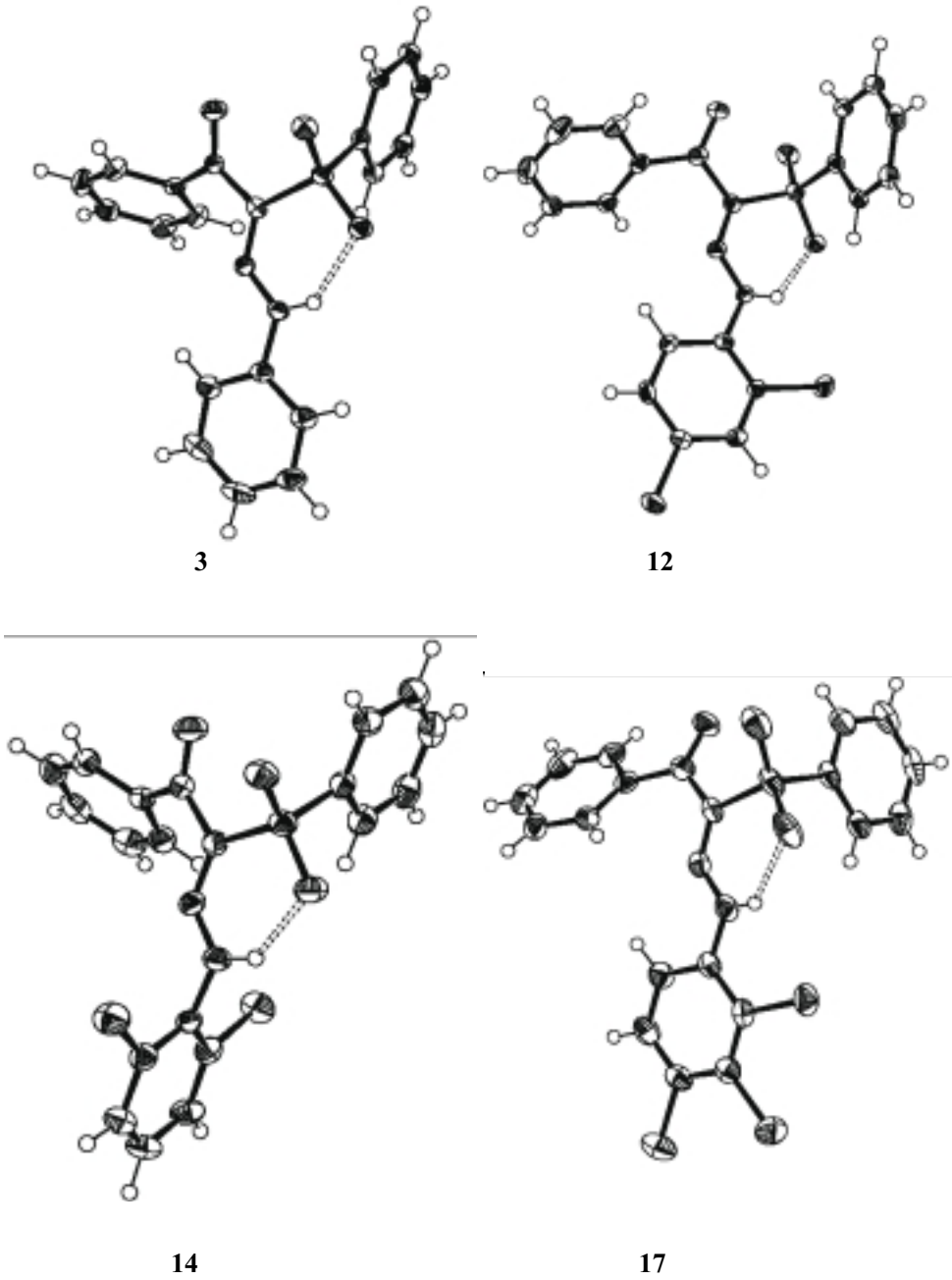


Figure 1. The ORTEP-3 [32] plots of the crystal structures of compounds **3**, **12**, **14** and **17**. The thermal ellipsoids are drawn by 50% probability level and the hydrogen bonds are shown as broken bars.

present in the molecule. Thus, the N–H...OS(O) resonance-assisted hydrogen bond in **HK1** is stronger than N–H...OC in **KH2**. It is clearly seen in Table 6 that structures that contain the (O)SO–H...N (**AE2**) and (O)SO–H...OC (**AE4**) are the least stable intra-molecular hydrogen bonds in the tautomeric forms considered (Scheme 3).

Table 6. Calculated relative energies [kJ/mol] for **3** and their tautomers.

Tautomer	HF/6-31G**[a]	MP2/6-31G**[a]
HK1	0.00	0.00
HK2	12.17	7.37
AK1	27.97	43.69
AE1	57.97	42.35
AE3	59.00	61.38
AE4	59.13	61.42
AE2	119.69	84.76
b	–1497.593161	–1501.209658

[a]PCM model of solvation (solvent: chloroform).
[b]Absolute energy [a.u.] of the most stable tautomer.

The results obtained allow us to conclude that **HK1** is the only tautomer present in chloroform solution of (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanones. Although the chemical shifts of H1, N1, and N2 were found to be linearly dependent on substituent constants, tautomeric preference is not affected by electron-withdrawing neither electron-donating groups. The N–H...OS(O) hydrogen bond in the respective tautomer seems to be much more strong than other hydrogen bonds present in the molecules of other tautomers. *Ab initio* calculations show that **HK1** is really the most stable tautomer.

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REFERENCES

1. Gawinecki R., Kolehmainen E., Janota H., Kauppinen R., Nissinen M. and Ośmiałowski B., *J. Phys. Org. Chem.*, **14**, 797 (2001).
2. Berger S., Braun S. and Kalinowski H-O., *NMR Spectroscopy of Non-Metallic Elements*, Wiley, Chichester, 1997, pp. 1020–1041.
3. Bassindale R. and Iley J.N., *The NMR and ESR Spectra of Sulphonic Acids and Their Derivatives in The Chemistry of Sulphonic Acids, Esters and Their Derivatives (The Chemistry of Functional Groups)*, Patai S. and Rappoport Z., Eds, Wiley, Chichester, 1991, pp. 197–247.
4. Basch H. and Hoz T., *General and Theoretical in The Chemistry of Sulphonic Acids, Esters and Their Derivatives (The Chemistry of Functional Groups)*, Patai S. and Rappoport Z., (eds), Wiley, Chichester, 1991, pp. 1–62.

5. Hoz T. and Basch H., *General and Theoretical in The Chemistry of Sulfur-Containing Functional Groups, Suppl. S (The Chemistry of Functional Groups)*, Patai S. and Rappoport Z., Eds, Wiley, Chichester, 1993, pp. 1–100.
6. Exner O., in *Correlation Analysis in Chemistry, Recent Advances*, Chapman N.B., Shorter J., Eds, Plenum Press, NY, 1978, p. 439.
7. Dal Colle M., Bertolasi V., de Palo M., Distefano G., Jones D., Modelli A. and Olivato P.R., *J. Phys. Chem*., **99**, 15011 (1995).
8. Krawiec M., Krygowski T.M. and Zakrzewski A., *Acta Cryst., Sect. C*, **45**, 345 (1989).
9. Kirby A.J., *The Anomeric and Related Stereoelectronic Effects at Oxygen; Reactivity and Structure Concepts on Organic Chemistry*, Vol. 15, Springer, Berlin, 1983.
10. *The Anomeric Effect and Associated Stereoelectronic Effects*, Thatcher G.R.J., Ed., American Chemical Society, Washington DC, 1993.
11. Wolf W.M., *J. Mol. Struct*., **474**, 113 (1999).
12. Borchardt A., Kopkowski A., Kornacki Z. and Zakrzewski A., *J. Chem. Soc., Perkin Trans. 2*, 845 (1990).
13. Gawinecki R., Kolehmainen E., Zakrzewski A., Laihia K., Ośmiałowski B. and Kauppinen R., *Magn. Reson. Chem*., **37**, 437 (1999).
14. Kolehmainen E., Janota H., Gawinecki R., Laihia K. and Kauppinen R., *Magn. Reson. Chem*., **38**, 384 (2000).
15. Zakrzewski A., *Przem. Chem*., **78**, 17 (1999); *Chem. Abstr.*, **130**, 267179y (1999).
16. Nepluev V.M., Sinenko T.A., Usenko Yu.N., Dubenko R.G. and Pelkis P.C., *Zh. Org. Khim*., **8**, 337 (1972).
17. Zakrzewski A., *Pestycydy (Warsaw)*, 63 (1998); *Chem. Abstr.*, **130**, 263451h (1999).
18. Shawali A.S.A.S., Ali M.I., Naoum M.M. and Elansari A.L., *Tetrahedron*, **28**, 3805 (1972).
19. Kolehmainen E., Ośmiałowski B., Krygowski T.M., Kauppinen R., Nissinen M. and Gawinecki R., *J. Chem. Soc., Perkin Trans. 2*, 1259 (2000).
20. Kolehmainen E., Ośmiałowski B., Nissinen M., Kauppinen R. and Gawinecki R.,*J. Chem. Soc., Perkin Trans. 2*, 2185 (2000).
21. Otwinowski Z. and Minor W., *Methods in Enzymology*, **276**, 307 (1997).
22. Sheldrick G.M., *SHELXS 97, A Program for Automatic Solution of Crystal Structures*, University of Göttingen, 1997.
23. Sheldrick G.M., *SHELXL 97, A Program for Crystal Structure Refinement*, University of Göttingen, 1997.
24. Hansch C., Leo A. and Taft R.W., *Chem. Rev.*, **91**, 165 (1991).
25. *Gaussian 98, Revision A.7*, Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery J.A., Jr., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford C., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Ortiz J.V., Baboul A.G., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Andres J.L., Gonzalez C., Head-Gordon M., Replogle E.S. and Pople J.A., Gaussian, Inc., Pittsburgh PA, 1998
26. Rance M., Sørensen O.W., Bodenhausen G., Wagner G., Ernst R.R. and Wüthrich K., *Biochem. Biophys. Res. Commun*., **117**, 479 (1984).
27. Derome A. and Williamson M., *J. Magn. Reson*., **88**, 117 (1990).
28. Bax A., Griffey R.H. and Hawkins B.L., *J. Magn. Reson*., **55**, 301 (1983).
29. Bax A. and Subramanian S., *J. Magn. Reson*., **67**, 565 (1986).
30. Bax A. and Summers M.F., *J. Am. Chem. Soc*., **108**, 2093 (1986).
31. Furukawa N. and Fujihara H., *Hydrogen Bonding and Complexing Properties of R_2SO_2 and R_2SO in The Chemistry of Sulphones and Sulphoxides (The Chemistry of Functional Groups)*, Patai S., Rappoport Z. and Stirling Sh., Eds, Wiley, Chichester, 1988, pp. 541–581.
32. Farrugia L.J., *J. Appl. Cryst.*, **30**, 565 (1997).