DIPOLE MOMENTS OF *para*-SUBSTITUTED *N*-PHENYLSULFONYL-*N*′-ALLYLTHIOUREAS

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Dipole moments of a series of *para*-substituted *N*-phenylsulfonyl-*N*′-allylthioureas were determined. Comparison of the experimentally found dipole moments with those calculated by vector addition of bond and group moments has shown that (*E*) conformation at the N–C bonds is preferred. The same result was obtained from the N–H stretching vibrations. The results are compatible with a synperiplanar arrangement at the C–C bond of the allyl moiety.

In our previous papers[1,2], studying reactivity and dipole moments of phenylsulfonyl isothiocyanates, we were interested mainly in the polar character of the SO_2 and CO groups and in the spatial arrangement of conformers arising by rotation around the bond between the sulfur and the trigonal nitrogen atoms. In this context, we also studied a representative series of *meta*- and *para*-substituted benzoyl isothiocyanates[3]. Within the framework of a complex investigation of arylsulfonyl derivatives, in this communication we have studied a series of *para*-substituted *N*-phenylsulfonyl-*N*′-allylthioureas *I* – *VI*. We were interested particularly in the preferred rotamers arising by rotation around the bonds S_7–N_8, N_8–C_9, C_9–N_{10} or N_{10}–C_{11}. This conformational analysis is based on comparison of dipole moments calculated by vector addition with those determined experimentally; we also have taken into consideration the wavenumbers of the N–H bonds. So far, no reports are known on conformational studies of *N*-phenylsulfonyl thioureas based on dipole moments and spectral properties. On the basis of X-ray diffraction studies[4] which unequivocally confirm the mesomeric structure of thioureas, and of spectral properties[5,6] of *N*-monosubstituted and *N*,*N*′-disubstituted thioureas, we did not consider any tautomerism.

EXPERIMENTAL AND CALCULATIONS

para-Substituted *N*-phenylsulfonyl-*N*′-allylthioureas were prepared by the described procedure[7]. Their dipole moments were determined in benzene at least at five concentrations in the region 0.01 – 0.08 mol/l. Benzene was of UV-spectral quality, distilled on a column (b.p. 80 °C), dried over molecular sieve

Nalsit-4 and passed through a column of activated alumina immediately before use. Permittivities of the studied compounds were measured on a Dipolmeter DM 01 instrument (Wissenschaftlich-technische Werkstatten, GmbH), accuracy 0.0001, frequency for liquids 2 MHz, temperature 20 ± 0.05 °C. The volume of thermostated cell DFL 2 was 4 ml. Density measurements were performed in 10 ml pyknometers for volatile compounds. Refractive indices were determined on an Abbe refractometer (Zeiss, Jena). Dipole moments were calculated according to Halverstadt and Kumler[8] with 5% correction for atomic polarization. Infrared absorption spectra were recorded on a Specord IR75 (Zeiss, Jena) spectrophotometer in the region 4 000 – 400 cm^{-1} (calibration with polystyrene); NaCl cells (thickness 0.17), solvent $CHCl_3$, concentration 0.05 mol/l. As seen from the concentration dependence, there was no intermolecular hydrogen bonding in solutions of the measured compounds.

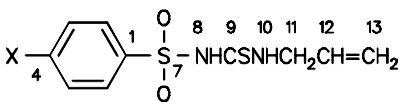
For calculations of the dipole moments using vector addition of bond or group moments we used the standard published values[9–11] (in 10^{-30} C m): H–C_{ar} 0.00; C_{ar}–Cl 5.29; C_{ar}–Br 5.23; C_{ar}–CH_3 1.23; C_{ar}–OCH_3 4.26 (Θ 72°); C_{ar}–$COCH_3$ 9.77 (Θ 132°); C–S 3.00; SO_2 10.67; conjugation correction for $ArSO_2$ 3.33; S–N 1.99; N–H 4.36; C–N 1.49; C=S 6.66; C_{al}–H 1.33; C_{sp^2}–C_{sp^3} 2.33. Bond angles[12,13]: C_{ar}–S–O 109°; O–S–O 119°; C_{ar}–S–N 105°; S_7–N_8–C_9 128°; S_7–N_8–H 116°; C_9–N_{10}–C_{11} 120°; N_{10}–C_{11}–C_{12} 109°; C_{11}–C_{12}–C_{13} 120°.

RESULTS AND DISCUSSION

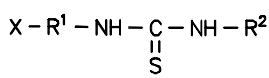
In order to compare the results of IR spectral measurements of *N*-phenylsulfonyl-*N*′-allylthioureas *I* – *VI* with those obtained from their dipole moments and from spectral measurements on *N*-phenylsulfonyl-*N*′-butylthioureas[2], *N*-phenylsulfonyl-*N*′-phenylthioureas and *N*,*N*′-diphenylthioureas *VII* – *XVI*, synthesized as models according to described procedures[4,14], it was necessary to find suitable conditions of the measurements and evaluation of their absorption spectra (Table I). Similarly to the case of diphenylthioureas *XV* and *XVI*, the two N–H bands in the spectra of *N*-phenylsulfonyl-*N*′-phenylthioureas *VII* – *XI* can be ascribed[5,6] to the (*E*) and (*Z*) planar conformations at the C–N bond. In the spectra of *N*-phenylsulfonyl-*N*′-allylthioureas *I* – *VI* and *N*-phenylsulfonyl-*N*′-butylthioureas *XII* – *XIV* the two N–H groups appear in chloroform as a single strong band which, according to the literature data[6], corresponds to conformation (*E*). In this context, it is interesting to compare the four possible planar conformations at the C–N bonds of *N*-phenylsulfonylthioureas *I* – *XIV*. As follows from the observed facts, the two N–H bands found for *N*-phenylsulfonyl-*N*′-phenylthioureas *VII* – *XI* and *N*,*N*′-diphenylthioureas *XV* and *XVI* correspond to planar arrangements (*E*,*Z*) or (*Z*,*E*) whereas the single band due to two N–H groups in *N*-phenylsulfonyl-*N*′-allylthioureas *I* – *VI* and *N*-phenylsulfonyl-*N*′-butylureas *XII* – *XIV* can be ascribed to planar (*E*,*E*) or (*Z*,*Z*) conformations. On the basis of our previous results[2] we can assume that the larger differences between the N–H absorption bands ($\Delta\nu$(NH) ≈ 100 cm^{-1}) for *N*-phenylsulfonyl-*N*′-phenylthioureas *VII* – *XI* compared with those for *N*,*N*′-diphenylthioureas *XV* and *XVI* ($\Delta\nu$(NH) ≈ 33 cm^{-1}) are due to the negative transmission effect of the SO_2 group, realized mainly by the π-inductive effect.

For *N*-phenylsulfonyl-*N′*-allylthioureas, we tried to decide between the (*E*,*E*) and (*Z*,*Z*) planar conformations by comparison of the experimental dipole moments with those calculated by vector addition. The dipole moments of *N*-phenylsulfonyl-*N′*-phenylthioureas could not be measured because of their very low solubility in benzene.

The experimental dipole moments for a series of *para*-substituted *N*-phenylsulfonyl-*N′*-allylthioureas (Table II) were compared with those calculated for the individual planar conformations *2* – *5* (Scheme 1) arising by gradual rotation about single bonds (N_8–C_9, C_9–N_{10}, N_{10}–C_{11}, C_{11}–C_{12}) of the parent structure *1* (Table I). This comparison has shown the preference of conformation *5* arising from conformation *4* by rotation around the C_{11}–C_{12} bond. The graphic method[15], employed for X = CH_3 and X = Cl (Fig. 1), confirmed the conformation *5* with synperiplanar arrangement of the allyl moiety. The same results were also obtained with compounds where X = Br, OCH_3 and $COCH_3$. For substituents with non-zero angle of the group moment (X = OCH_3,



	X
I	OCH_3
II	CH_3
III	H
IV	Cl
V	Br
VI	$COCH_3$



	X	R^1	R^2
VII	H	$C_6H_4SO_2$	C_6H_5
VIII	OCH_3	$C_6H_4SO_2$	C_6H_5
IX	CH_3	$C_6H_4SO_2$	C_6H_5
X	Cl	$C_6H_4SO_2$	C_6H_5
XI	Br	$C_6H_4SO_2$	C_6H_5

	X	R^1	R^2
XII	H	$C_6H_4SO_2$	*n*-C_4H_9
XIII	CH_3	$C_6H_4SO_2$	*n*-C_4H_9
XIV	Cl	$C_6H_4SO_2$	*n*-C_4H_9
XV	Br	C_6H_4	C_6H_5
XVI	CH_3	C_6H_4	C_6H_5

TABLE I

Infrared spectra (cm^{-1}) of *N*-phenylsulfonyl-*N*′-allylthioureas *I – VI*, *N*-phenylsulfonyl-*N*′-phenylthioureas *VII – XI*, *N*-phenylsulfonyl-*N*′-butylthioureas *XII – XIV* (ref.[2]) and *N*,*N*′-diphenylthioureas *XV* and *XVI* in chloroform

Compound	ν(NH)			ν(SO_2)	
	(*E*)	(*Z*)	Δν(NH)	ν_s	ν_{as}
I	3 347			1 152	1 384
II	3 366			1 150	1 387
III	3 366			1 150	1 387
IV	3 346			1 150	1 380
V	3 348			1 151	1 380
VI	3 350			1 150	1 386
VII	3 357	3 457	100	1 173	1 357
VIII	3 360	3 457	97	1 173	1 360
IX	3 357	3 453	96	1 173	1 350
X	3 346	3 450	104	1 166	1 350
XI	3 346	3 450	104	1 166	1 350
XII	3 319			1 119	1 376
XIII	3 350			1 119	1 376
XIV	3 349			1 141	1 369
XV	3 370	3 403	33		
XVI	3 378	3 405	27		

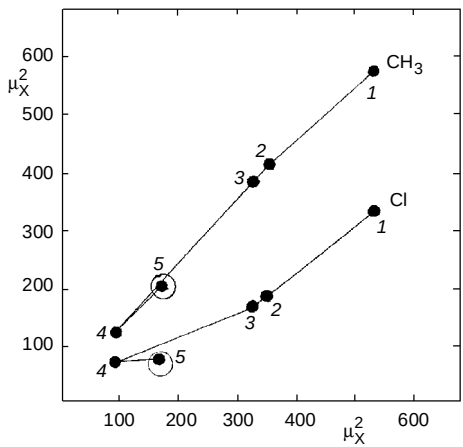


FIG. 1

Graphical comparison of squared dipole moments of *para*-substituted *N*-phenylsulfonyl-*N*′-allylthioureas; *x*-axis: X = H, *y*-axis: X = CH_3 or Cl

$COCH_3$), the conformation *b* is preferred to conformation *a* (Scheme 1, Table II). For substituents with zero angle of group moment we used the graphic method[16] to estimate the direction and magnitude of dipole moment of the SO_2–NH–CS–NH–allyl moiety. The obtained values were $\mu(SO_2NHCSNHAllyl) = 12.54 \cdot 10^{-30}$ C m and $\Theta = 21°$. Similar values ($12.38 \cdot 10^{-30}$ C m and 21.5°) were obtained by using the optimization condition (*1*):

$$\sum_{i=1}^{n} [\mu(i) - \mu_a(i)]^2 = \text{min.} \,, \qquad (1)$$

where $\mu(i)$ are the experimentally determined dipole moments of selected *para*-substituted derivatives and $\mu_a(i)$ are the corresponding values of dipole moments obtained by vector addition of the group moments.

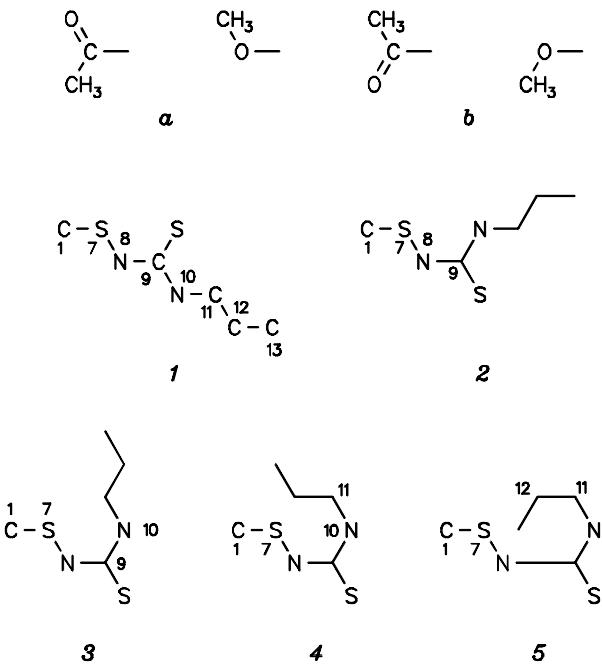
In our IR spectral studies on sulfonylthioureas (Table I) we were also interested in the SO_2 absorption bands in connection with the search for linear relationships between $\nu(SO_2)$ and substituent effects or between the S–O bond length and the O–S–O angles in compounds of the type Y_1–SO_2–Y_2 (refs[17,18]). It appeared that, in spite of very small

TABLE II
Experimental slopes of the concentration dependences of permittivities (α), densities (β) and refractive indices (γ), and calculated dipole moments (μ, 10^{-30} C m) of *para*-substituted *N*-phenylsulfonyl-*N'*-allylthioureas *I* – *VI*

Compound	α	β	γ	μ_{exp}	μ_{calc}					
					1	*2*	*3*	*4*	*5*	free rotation
I	31.24	1.18	0.89	15.03	24.15	19.96	19.30	10.89 9.90[b] 12.70[c]	14.68[a] 12.87[b] 16.33[c]	12.87
II	25.70	1.24	0.75	13.64	24.10	19.80	19.14	10.89	13.86	12.54
III	24.01	1.01	0.64	13.25	22.77	18.48	17.82	9.57	12.87	11.55
IV	8.60	0.49	0.82	7.44	18.15	13.20	12.54	5.28	9.07	7.26
V	9.43	0.56	0.83	7.84	18.97	13.53	13.20	5.61	9.24	6.76
VI	5.91	1.04	0.96	5.87	17.32	12.11	11.88	4.45 11.30[b] 4.78[c]	8.58[a] 15.84[b] 3.13[c]	6.93

[a] Free rotation. [b,c] Values for conformers *a* and *b* (Scheme 1), respectively.

changes in empirical constants of substituents Y_1 and Y_2 (Y_1 = C_6H_5, Y_2 = NH–CS–NHR), the experimental values of wavenumbers $\nu_{as}(SO_2)$ or $\nu_s(SO_2)$ differ for the individual sulfonylthioureas. This fact is probably connected with a different interaction of the SO_2 group with substituents Y_1 and Y_2 in the mentioned series of *N*-phenylsulfonylthioureas which should manifest itself by change in structure of the SO_2 group. Using the published correlations[18], we calculated from the value ($\nu_{as}(SO_2)$ + $\nu_s(SO_2)$)/2 = 1 265 cm^{-1} that the S–O bond length is 143 pm, its order is 1.81, and the O–S–O angle is 119°.



SCHEME 1

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