

A STUDY OF DIPOLE MOMENTS OF SUBSTITUTED ISOTHIOCYANATES OF 1,3-DIPHENYL-2-PROPEN-1-ONE

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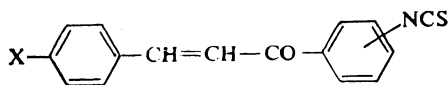
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Received November 15th, 1983

The dipole moments have been measured of various substituted isothiocyanates of 1,3-diphenyl-2-propen-1-one in benzene solution. The measured values have been compared with the dipole moments obtained by the vector addition of the bond dipole moments, and the comparison has been used for a discussion of their electronic structure and interactions of the NCS group.

The available literature¹⁻⁴ gives the dipole moments of monosubstituted derivatives of 1,3-diphenyl-2-propen-1-ones and their quinoline analogues. In the field of isothiocyanates, the dipole moments of phenyl isothiocyanates are described in ref.⁵, 4-substituted 3-phenylpropenoyl isothiocyanates in ref.⁶, and spectral properties of substituted isothiocyanates of 1,3-diphenyl-2-propen-1-ones in refs^{7,8}.

The aim of the present communication is a study of dipole moments of various substituted isothiocyanates of 1,3-diphenyl-2-propen-1-ones and elucidation of their structure, steric arrangement, and electronic interactions with the NCS group.



Ia - j

I, 4-NCS; *a*, X = H; *b*, X = CH₃O; *c*, X = CH₃; *d*, X = Cl; *e*, X = Br; *f*, X = NCS; *g*, X = NO₂
I, 3-NCS; *h*, X = H; *i*, X = CH₃O; *j*, X = Cl

EXPERIMENTAL

Reagents: 1-(4-isothiocyanatophenyl)-3-phenyl-2-propen-1-one (*Ia*), m.p. 123–124.5°C; 1-(4-isothiocyanatophenyl)-3-(4-methoxyphenyl)-2-propen-1-one (*Ib*), m.p. 138–140°C; 1-(4-isothiocyanatophenyl)-3-(4-methylphenyl)-2-propen-1-one (*Ic*), m.p. 133.5–135°C; 1-(4-isothiocyanatophenyl)-3-(4-chlorophenyl)-2-propen-1-one (*Id*), m.p. 119–121°C; 1-(4-isothiocyanatophenyl)-3-bromophenyl)-2-propen-1-one (*Ie*), m.p. 138–140°C; 1,3-bis(4-isothiocyanatophenyl)-2-propen-1-one (*If*), m.p. 148.5–149°C (1-(4-isothiocyanatophenyl)-3-(4-nitrophenyl)-2-pro-

pen-1-one (*Ig*), m.p. 144–145°C; 1-(3-isothiocyanatophenyl)-3-phenyl-2-propen-1-one (*Ih*), m.p. 104–105°C; 1-(3-isothiocyanatophenyl)-3-(4-methoxyphenyl)-2-propen-1-one (*Ii*), m.p. 98.5 to 100°C; 1-(3-isothiocyanatophenyl)-3-(4-chlorophenyl)-2-propen-1-one (*Ij*), m.p. 113.5–114°C; 1-phenyl-3-(4-isothiocyanatophenyl)-2-propen-1-one (*Ila*), m.p. 130.5–132°C; 1-(4-methoxyphenyl)-3-(4-isothiocyanatophenyl)-2-propen-1-one (*Ilb*), m.p. 149.5–151°C; 1-(4-chlorophenyl)-3-(4-isothiocyanatophenyl)-2-propen-1-one (*Ilc*), m.p. 146–148°C; 1-phenyl-3-(3-isothiocyanatophenyl)-2-propen-1-one (*Ild*), m.p. 86.5–87°C; 1-(4-methoxyphenyl)-3-(3-isothiocyanatophenyl)-2-propen-1-one (*Ile*), m.p. 125.5–126.5°C; 1-(4-chlorophenyl)-3-(3-isothiocyanatophenyl)-2-propen-1-one (*Ilf*), m.p. 143–144°C all were described in refs^{7,8}.

Dipole moments: The dipole moments were measured in benzene solutions with the concentrations of the above-given compounds within the limits from 0.015 to 0.080 mol l⁻¹. The benzene used was of UV-spectral purity grade and was dried over sodium metal and distilled through a column (b.p. 80.1°C). It was kept over the molecular sieve Nalsit-4 and was passed through an activated alumina column before use. The dielectric constants of the solutions investigated were measured with a Dipolmeter type DM 01 apparatus (Wissenschaftlich-Technische Werkstätten, FRG) with the accuracy of 0.0001 unit. The temperature during the measurements was 20 + 0.05°C. The specific frequency of the apparatus was 2 MHz for liquids. The measurements were carried out in tempered cells DFL 2 of 4 ml volume. The density was determined in 10 ml pycnometers designed for volatile substances. The refractive index was measured with the Abbe immersion refractometer (Zeiss, Jena).

Calculation of the dipole moments: The dipole moment values were calculated according to both Halverstadt and Kumler⁹ and Guggenheim and Smith^{10–12} without correction to atomic polarisation. The following values of the bond dipole moments (in Cm) were used for the theoretical calculations: >C=O 9.005 · 10⁻³⁰; C_{Ar}-CH₃ 1.334 · 10⁻³⁰; C_{Ar}-OCH₃ 4.169 · 10⁻³⁰; C_{Ar}-Cl 5.269 · 10⁻³⁰; C_{Ar}-Br 5.336 · 10⁻³⁰; C_{Ar}-NO₂ 13.173 · 10⁻³⁰ (ref.³); C_{Ar}-NCS 9.705 · 10⁻³⁰ (ref.¹³). The angles C=C-C and C-C=O in the aliphatic chain 120° (ref.¹⁴); those of the group dipole moments Ar-OCH₃ θ = 72°, Ar-NCS θ = 20° (ref.⁵). The final dipole moment was calculated with the presumption of equal population of individual conformers according to Eq. (1).

$$\mu_{\text{calc}} = (\mu_1^2/n + \mu_2^2/n + \dots + \mu_n^2/n)^{1/2} \quad (1)$$

The distances (in nm) between the centre of aromatic nucleus and centre of the substituent charge: d_{H} 0.248; d_{CH_3} 0.355; $d_{\text{CH}_3\text{O}}$ 0.277; d_{Cl} 0.309; d_{Br} 0.328; d_{NO_2} 0.343 (ref.¹⁵). The Hammett σ_p constants: NO₂ 0.778; Br 0.230; Cl 0.227; CH₃ 0.170; CH₃O 0.268 (ref.¹⁶). The linear dependences were calculated according to Eqs (2) and (3).

$$\mu_{\text{R}} = (10.239 - 15.841\sigma_p) \cdot 10^{-30}, \quad r = 0.989 \quad (2)$$

$$(\mu_{\text{R}} - \mu_{\text{H}})/d_{\text{R}} = (-2.668 - 51.359\sigma_p) \cdot 10^{-30}, \quad r = 0.980 \quad (3)$$

RESULTS AND DISCUSSION

Table I gives the results of the measurements and values of the dipole moments measured and calculated for the investigated 1,3-diphenyl-2-propen-1-ones. The experimental dipole moment values obtained according to Guggenheim and Smith agree well with those according to Halverstadt and Kumler. For comparison we also

measured the dipole moment of 1,3-diphenyl-2-propen-1-one whose value $\mu = 10.27 \cdot 10^{-30}$ Cm agrees well with literature data¹⁻³. From the point of view of their configuration the substituted isothiocyanates are *trans* isomers with possible existence of two conformers: *s-cis* and *s-trans*. The calculation of dipole moments showed that the values of the two said conformers are equivalent, their dipole moments depending only on the conformation of the groups bound at the *para* and *meta* positions of the aromatic nuclei (Scheme 1). Besides that they are also dependent on the electron-donor and electron-acceptor properties of the substituents.

The dipole moments of the individual conformers of the functional groups indicate that the conformer 1 is predominant in the derivatives *Ia,c,d,e,g, IIc*. In the derivative *IIa* the both conformers 1 and 2 are present in equal amounts. With respect to the greater number of the mutual conformers of SCN-W-NCS and CH₃O-W-NCS groups (derivatives *Ib,f, IIb*) it is more difficult to determine the predominant one, but from the values it is obvious that 3 and 4 conformers are decisive. The dipole

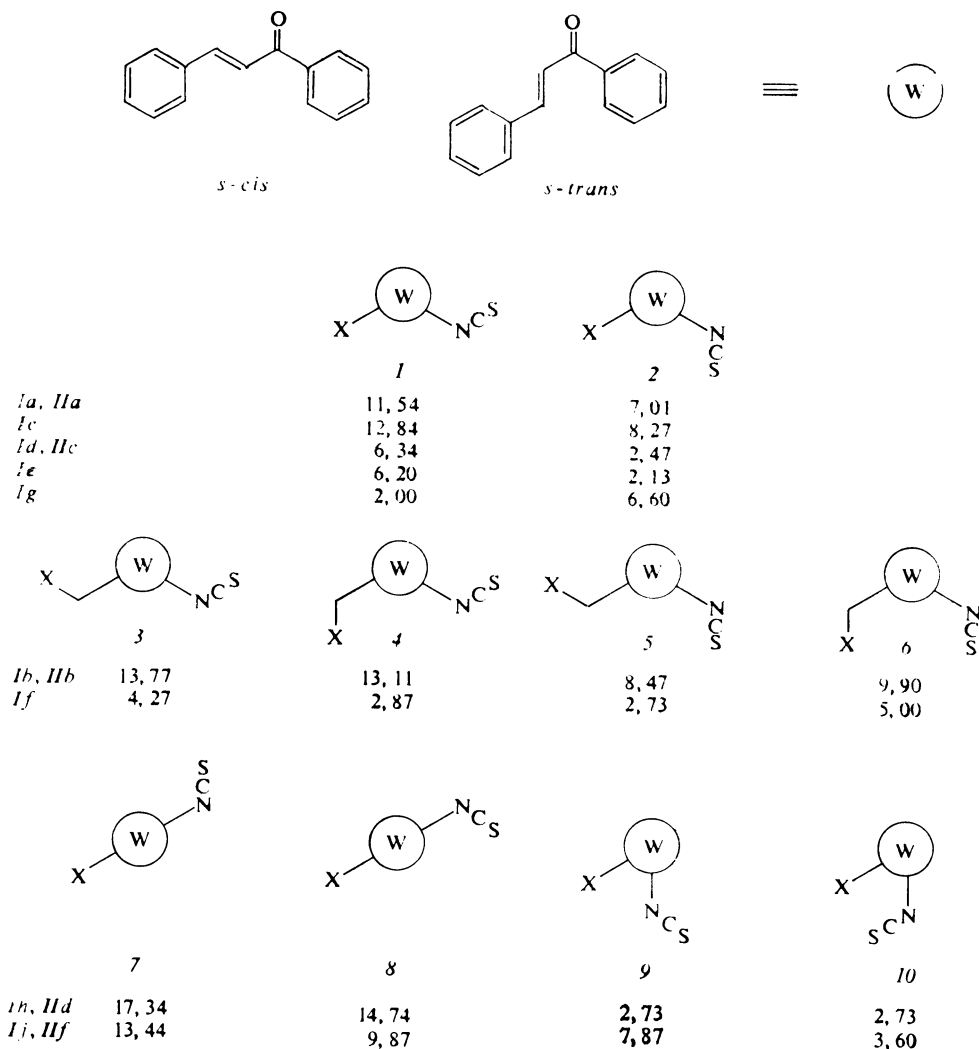
TABLE I
Polarization (cm³) and dipole moments μ (10^{-30} Cm) of substituted isothiocyanates of 1,3-diphenyl-2-propen-1-ones in benzene at 20°C

Compound	d_e	β_d	γ	∞P_2	R_D	μ_{exp}		μ_{calc}
						<i>a</i>	<i>b</i>	
<i>Ia</i>	17.83	0.814	1.900	325.1	92.7	11.14	11.26	9.51
<i>Ib</i>	28.72	0.981	2.221	489.5	102.9	14.37	14.65	11.51
<i>Ic</i>	23.00	0.873	2.000	399.9	93.0	12.79	12.94	11.34
<i>Id</i>	7.66	1.070	1.872	181.2	96.3	6.78	7.09	4.80
<i>Ie</i>	7.04	1.556	2.256	172.7	102.4	6.16	6.40	4.64
<i>If</i>	5.21	1.176	2.920	150.1	116.2	4.24	4.06	3.97
<i>Ig</i>	5.05	1.052	2.847	147.4	114.7	4.17	4.14	4.87
<i>Ih</i>	19.20	0.825	1.722	344.6	89.8	11.67	11.99	11.54
<i>Ii</i>	26.50	0.993	1.840	456.9	96.9	13.87	13.95	12.97
<i>Ij</i>	13.64	1.063	1.864	268.6	96.3	9.61	9.73	9.37
<i>IIa</i>	13.62	0.838	1.957	263.2	92.8	9.54	9.74	9.51
<i>IIb</i>	21.36	0.964	2.214	382.3	103.3	12.21	12.46	11.51
<i>IIc</i>	6.51	1.055	2.014	164.9	98.8	5.94	5.94	4.80
<i>IId</i>	17.72	0.841	1.699	323.4	88.9	11.21	11.24	11.54
<i>IIe</i>	23.56	1.025	1.876	412.9	96.5	13.01	13.13	12.97
<i>IIf</i>	13.38	1.162	0.805	261.6	92.5	9.51	9.72	9.37

^a The dipole moments according to Halverstadt and Kumler⁹ and ^b those according to Guggenheim and Smith¹⁰⁻¹².

moment values of the derivatives *Ih,j, IId,f* having the NCS group at the *meta* position of the aromatic ring indicate that 8 and *g* are the predominant conformers.

Theoretical values of dipole moments $\mu(10^{-30} \text{ Cm})$ of conformation of substituted isothiocyanates of 1,3-diphenyl-2-propen-1-ones

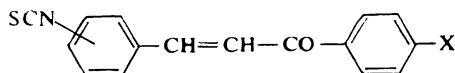


For conformers of derivatives *Ii—IIe* are the values of dipole moments as follows: 20·94; 16·37; 17·70; 15·10; 5·24; 3·23; 4·24; 6·57.

SCHEME 1

The given facts show that the differences between the measured and the calculated values of dipole moments are due to changes in population of the individual conformers of the groups attached to the aromatic nuclei, which is a result of the interaction between carbonyl and NCS groups. In case of the *Ia,b,d* derivatives the same reason also explains their higher values of the measured dipole moments as compared with those of the derivatives *Ila-Ilc*. An analogous situation is also encountered when comparing the derivatives *Ih-Ij* with *IId-f*.

From the linear dependences (2) and (3) between the dipole moments of the substituted isothiocyanates of 1,3-diphenyl-2-propen-1-ones (derivatives *Ia-Ig*) and the intramolecular distances d_R , respectively, and the σ_p constants of the substituents we calculated the values $\sigma_{\text{pNCS}} = 0.38$ and $d_{\text{NCS}} = 0.310$ nm, the former value being in good agreement with literature data^{17,18}.



II, 4-NCS; *a*, X = H; *b*, X = CH₃C; *c*, X = Cl
II, 3-NCS; *d*, X = H; *e*, X = CH₃O; *f*, X = Cl

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Translated by J. Panchartek.