DIPOLE MOMENTS AND CONFORMATION
OF CINNAMOYL ISOTHIOCYANATES*

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Dipole moments of 4-substituted cinnamoyl isothiocyanates in benzene were determined. Dipole moments of Z- and E-conformations of the above compounds were calculated by vector addition of the bond moments. The experimental dipole moments, as well as moments obtained using a graphical method, showed unequivocally that cinnamoyl isothiocyanates exist in Z-conformation with the torsion angle O==C—N==C 53°. The moment of the isothiocyanatocarbonyl group —CONCS was found to be 3·43 D with a 25° angle relative to the C—C bond.

In our previous papers we studied dipole moments of phenyl isothiocyanates and phenyl isoselenocyanates. The obtained results were used in the determination of polarity and geometry of the NCS and NCSe groups[1,2]. Recently, we turned our attention to the study of structure and reactions of cinnamoyl isothiocyanates which are highly reactive in nucleophilic additions and cycloadditions[3,4]. In connection with the study of these reactions it appeared desirable to obtain information on steric arrangement and the electronic character of the isothiocyanatocarbonyl group. In the present communication we determined dipole moments of some 4-substituted cinnamoyl isothiocyanates in order to study their structure and conformation, and electronic interactions of the —CONCS group with an aromatic moiety.

EXPERIMENTAL

Compounds. Cinnamoyl isothiocyanate (*I*), m.p. 41—43°C; 4-methylcinnamoyl isothiocyanate (*II*), m.p. 46—47°C; 4-chlorocinnamoyl isothiocyanate (*III*), m.p. 106—108°C; 4-bromocinnamoyl isothiocyanate (*IV*), m.p. 107—109°C; 4-cyanocinnamoyl isothiocyanate (*V*), m.p. 133—134°C; all these compounds were described in a previous work[3] and all are *trans*-isomers[3].

Dipole moments. Dipole moment measurements were carried out in $1·1-5·7 . 10^{-3}$ mol/l benzene solutions. Benzene was of UV-spectrograde purity and was dried over metallic sodium and distilled on a column (b.p. 80·1°C/760 Torr). It was stored over molecular sieve Nalsit-4 and passed before measurement through an activated alumina column. Dielectric constants

of the solutions were measured on a Dipolmeter DM 01 (Wissenschaftliche-Technische Werk-stätten, G.m.b.H.), accuracy 0·0001. Temperature of the system was 20 ± 0·05°C, the frequency for liquids was 2 MHz. The measurements were carried out in a thermostated DFL 2 cuvette, volume 4 ml. Density was determined in 10 ml pycnometers for volatile compounds. Refraction index was measured on an Abe immersion refractometer (Zeiss, Jena).

Calculation of dipole moments. The experimental dipole moments were calculated according to Halverstadt and Kumler[5] with a correction for the atomic polarisation $5-15\%$ R_D. For the calculation of configuration and conformation of 4-substituted cinnamoyl isothiocyanates the dipole moments were computed by vector addition of bond moments. Following values of the bond moments (in D) were used: $C=O$ 2·5; $C-N$ 0·45, $C_{ar}-CH_3$ 0·37, $C_{ar}-Cl$ 1·60, $C_{ar}-Br$ 1·58, $C_{ar}-CN$ 4·05 (ref.[6]); angles: $\sphericalangle\ C-C=O$ 120°, $\sphericalangle\ C-C-N$ 115°, $\sphericalangle\ N-C=O$ 125° (ref.[6,7]) $\sphericalangle\ C-N-C$ 140° (ref.[8]). The bond moment for the NCS group was calculated from the known dipole moments of methyl isothiocyanate[9] and phenyl isothiocyanate[1] and an average value was taken (NCS 2·52 D). The summation was made graphically (1 D = 3 cm) with an approximate accuracy ± 0·03 D.

RESULTS AND DISCUSSION

The found values of dipole moments, together with the values calculated for the both possible conformers, are listed in Table I. As seen from the Table, the isothiocyanato-
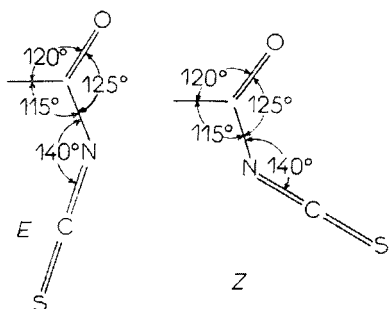

Fig. 1

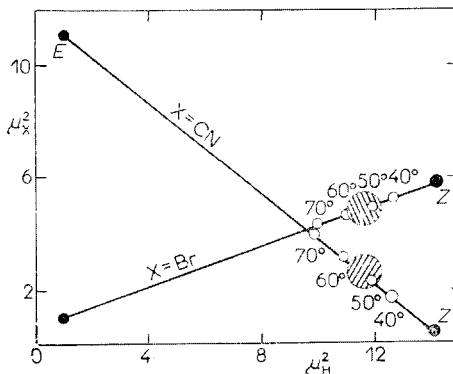Conformers of Cinnamoyl Isothiocyanates

Fig. 2

Graphical Comparison of the Calculated and Found Dipole Moments of Cinnamoyl, 4-Bromocinnamoyl and 4-Cyanocinnamoyl Isothiocyanates

The abscissa represents μ_H^2 for the unsubstituted compound, on the ordinate axis μ_X^2 values for 4-substituted derivatives are given. The calculated values for the E and Z conformers are depicted by empty circles (for an angle 140°); the experimental value is hatched.

carbonyl group is a relatively strong electron acceptor, so that the direction of the dipole is reversed only in 4-cyanocinnamoyl isothiocyanate where the negative charge is situated at the —C≡N group.

In contrast to phenyl isothiocyanates, we can anticipate two possible conformations, Z or E, for acyl isothiocyanates (Fig. 1). A cinnamoyl isothiocyanate molecule can exist in two configurations about the C=C bond and in two conformations about the C—C and C—N bonds. The configuration of the C=C bond is known from previous studies[3,10] and the present paper deals with the conformation of the C—N bond. The conformation about the C—C bond in *para*-substituted derivatives cannot be deduced from the dipole moments. Dipole moments of the Z and E conformations of 4-substituted cinnamoyl isothiocyanates were calculated by vector addition of the bond moments. It is evident at the first sight (Table I) that the found dipole moments correspond to that calculated for the Z conformation. This was confirmed also by a graphical method consisting in a systematic comparison of the dipole moment of the substituted and unsubstituted compound[7,11] (Figs 2 and 3). The results of this method confirm that all measured cinnamoyl isothiocyanates exist in the Z conformation with a torsion angle O—C—N=C 53°.

We determined further the moment of the isothiocyanatocarbonyl group using the graphical method described by van Voerden and Havinga[12]. The obtained experimental values of dipole moments of cinnamoyl isothiocyanates were plotted
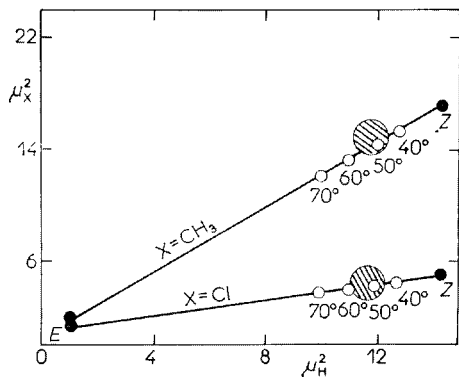

FIG. 3

Graphical Comparison of the Calculated and Experimental Dipole Moments of Cinnamoyl Isothiocyanate with That of 4-Methylcinnamoyl and 4-Chlorocinnamoyl Isothiocyanates
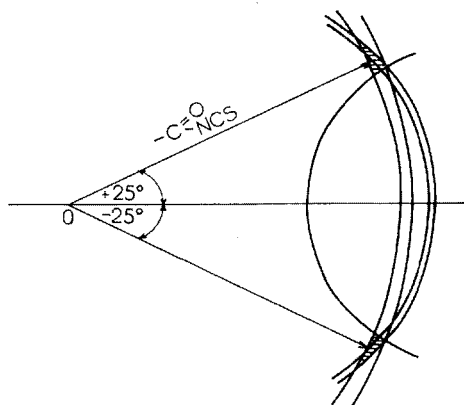
For description see Fig. 2.

FIG. 4

Determination of the Group Moment of the —CONCS Group

For description of the method see p. 744.

TABLE I

Polarisation (cm^3) and Dipole Moment (D) Values Found for Cinnamoyl Isothiocyanates $I-V$ in Benzene at 20°C

Com-pound	α_ε	α_{n^2}	β_d	$_\infty P_2$	R_D	μ, 5%	μ, 15%	μ (calc.)	
								Z	E
I	17·64	0·934	0·576	304·1	60·3	3·40	3·36	3·77	1·02
II	22·69	1·068	0·593	381·1	66·2	3·87	3·83	4·15	1·30
III	7·82	1·197	0·812	165·4	68·5	2·12	2·04	2·20	1·10
IV	8·16	1·283	1·344	169·3	68·9	2·16	2·08	2·42	1·00
V	5·04	1·162	0·755	120·5	63·5	1·61	1·51	0·75	3·34

as circles the centers of which were obtained by plotting of bond moments of the substituents from the origin. The tie-line connecting the origin with the center of the area of the intersecting circles represents the bond moment of the isothio-cyanatocarbonyl group (Fig. 4). Thus we obtained for —CONCS group the moment 3·43 D with the angle 25° relative to the double bond. This value must be considered only as approximate because the circles were not intersected exactly in one point; however, a better accuracy cannot be expected.

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