DIPOLE MOMENTS OF meta AND para SUBSTITUTED BENZOYL ISOTHIOCYANATES

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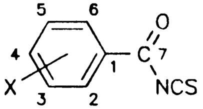
For a series of meta and para substituted benzoyl isothiocyanates, the dipole moments were determined experimentally and calculated by vector addition of the bond and group dipole moments. Conformation analysis revealed the preference of the synclinal conformation (τ ≈ 60°), which emerges from the rotation about the C(7)–N bond. MNDO calculations were also performed for the compounds, and the dipole moments obtained were compared with those from the above procedure.

Previously[1,2] we investigated the dipole moments of heterocumulenes of the R–NCY type (Y = O, S, Se). Attention in this respect was also devoted to a limited set of para substituted benzoyl isothiocyanates[3]. These dipole moments as well as those obtained for para substituted cinnamoyl isothiocyanates[4] and diphenylcarbonyl isothiocyanates[5], were employed for the study of their conformation. In the present work, a representative series of meta and para substituted benzoyl isothiocyanates (Scheme 1) was examined. In the case of meta substituted benzoyl isothiocyanates, whose dipole moments have not yet been determined, the effect of the substitutents on the spatial arrangement of the –CONCS group with respect to the substituted aromatic ring was of major interest. Another problem of interest was the relation between the experimental dipole moments and those calculated by the MNDO method for the above compounds.



X = $N(CH_3)_2$, OCH_3, CH_3, C_6H_5, H, F, Cl, Br, CN, NO_2

SCHEME 1

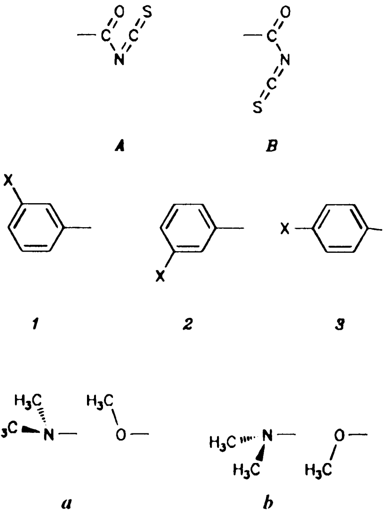
EXPERIMENTAL AND CALCULATIONS

Meta and para substituted benzoyl isothiocyanates were prepared as described previously[6]. Their dipole moments were determined in benzene solutions at a minimum of five concentrations over the 0.01 to 0.08 mol dm^{-3} range. Benzene for UV spectroscopy was redistilled on a column (b.p. 80.1 °C) and dried over Nalsit-4 molecular sieve, and immediately prior to the measurement, passed through a column of activated Al_2O_3. Permittivities of the substances were measured on a Dipolmeter DM 01 instrument (Wissenschaftlich-technische Werkstätten GmbH) with a precision of 0.0001. The measuring frequency of the instrument for liquids was 2 MHz and the temperature of the system measured was 20 ± 0.05 °C. The measuring volume of the DFL 2 thermostatted cell was 4 ml. Densities were measured in 10 ml pycnometers for volatile substances, refractive indices were measured on an immersion Abbe refractometer (Zeiss, Jena). The dipole moments were calculated using the method by Halverstadt and Kumler[7] with a 5% correction for atomic polarization.

The dipole moment calculations based on vector addition of bond and group moments were made using published standard values[3,4,8–13], viz. (in 10^{-30} C m): H-C(ar) 0.0, C(ar)-Cl 5.29, C(ar)-Br 5.23, C(ar)-F 4.89, C(ar)-CN 13.49, C(ar)-NO_2 13.36, C(ar)-CH_3 1.23, C(ar)-OCH_3 4.26 (Θ 72°), C(ar)-$N(CH_3)_2$ 5.26 (Θ 34°), -NCS 8.4, -CONCS 10.96 (Θ 16°), C=O 8.33. Bond angles: C(ar)-C=O 120°, C(ar)-C-N 115°, N-C=O 125°, C-N-C 140°. The quantum chemical calculations were performed by using the MNDO method[14]; all angles and bond lengths were optimized.

RESULTS AND DISCUSSION

The dipole moments and the results of measurement are given in Tables I and II. For the meta substituted benzoyl isothiocyanates, the planar arrangement of the dipole moments of the functional groups and bonds determines four conformers (A_1, A_2, B_1, B_2) in the case of substituents with a zero angle of the group dipole moment (X = CH_3, F, Cl, Br, CN, NO_2), and eight conformers (A_1^a, A_2^a, B_1^a, B_2^a, A_1^b, A_2^b, B_1^b, B_2^b) in the case of substituents with a nonzero angle of the group dipole moment (X = $N(CH_3)_2$, OCH_3) (Scheme 2). Of interest were the preferred conformations of the meta substituted



SCHEME 2

TABLE I

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 meta substituted benzoyl isothiocyanates and unsubstituted benzoyl isothiocyanate

X	α	β	γ	μ_{exp}	μ_a				μ_{MNDO}		
					A_1	B_1	A_2	B_2	μ_{chg}	μ_{hyb}	μ_{sum}
$N(CH_3)_2$	22.48	0.461	0.784	12.84	12.50^a 17.20^b	7.80^a 8.60^b	14.20^a 17.80^b	3.80^a 7.31^b	12.62	4.44	16.76
OCH_3	15.02	0.555	0.668	10.47	9.60^a 17.02^b	5.14^a 6.91^b	11.10^a 16.75^b	2.10^a 7.81^b	12.34	2.53	14.72
CH_3	18.18	0.566	0.781	11.54	13.07	4.47	13.47	3.30	12.72	2.51	14.93
F	11.86	0.681	0.808	9.18	11.98	2.10	10.09	6.36	9.83	2.57	11.97
Cl	10.66	0.795	0.946	8.59	12.00	2.45	9.96	6.71	9.84	2.68	12.04
Br	11.69	0.967	1.161	8.93	12.01	2.40	9.98	6.71			
CN	20.99	0.892	0.850	12.43	15.22	10.95	10.80	14.44	17.13	5.79	21.02
NO_2	19.81	0.884	0.857	12.05	15.14	10.32	10.74	14.32	13.66	2.96	15.83
H	16.11^c	0.402^c	0.614^c	10.94^c	12.62^c	3.29^c					

[a,b] Values for the conformers labelled *a* and *b*, respectively; [c] ref.[3]. The subscripts exp, a, chg, hyb and sum refer to values determined experimentally, by vector addition, for the pure charges, hybrid and their sum, respectively. The standard deviation of the experimental values is ±0.16 . 10^{-30} C m.

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 benzoyl isothiocyanates

X	α	β	γ	μ_{exp}	μ_a		μ_{MNDO}		
					A_3	B_3	μ_{chg}	μ_{hyb}	μ_{sum}
$N(CH_3)_2$	31.05	0.569	0.456	15.33	16.75^a 17.55^b	8.70^a 6.90^b	14.60	2.16	16.55
OCH_3	23.25^c	0.695^c	0.730^c	13.20^c	$13.62^{a,c}$ $14.85^{b,c}$	$7.35^{a,c}$ $4.38^{b,c}$	16.00	2.18	18.18
CH_3	18.69^c	0.557^c	0.651^c	11.80^c	13.69^c	4.29^c	13.05	2.32	15.08
C_6H_5	17.79^d	0.802^d	1.396^d	11.20^d	12.60^d	3.47^d	13.93	2.47	16.14
F	6.37	0.633	0.902	4.41	7.75	3.35	5.59	2.51	7.99
Cl	6.75^c	0.860^c	0.755^c	6.73^c	7.35^c	3.49^c	5.77	2.70	8.35
CN	4.28	0.850	0.937	4.97	2.40	11.20	3.13	1.53	3.58
NO_2	4.47^c	0.880^c	0.399^c	5.53^c	2.64^c	10.89^c	6.16	2.57	4.43

[a,b,c] As in Table I; [d] ref.[5].

benzoyl isothiocyanates, formed by rotation about the C(7)–N, C(ar)–C(7) bonds, or the C(ar)–N, C(ar)–O bonds. These were analyzed by comparing the dipole moments calculated by vector addition for the conformations formed by the above rotation with those determined experimentally. For this, the sinusoidal dependence of the calculated dipole moments squared on the dihedral angle τ as well as the graphic method[10] were employed. The comparison revealed that the synclinal conformation of benzoyl isothiocyanate and *p*-cyanobenzoyl isothiocyanate (Fig. 1) formed by rotation about the C(7)–N bond, with a dihedral angle τ about 60°, is preferred. The preferred synclinal conformation for the meta substituted benzoyl isothiocyanates is corroborated by the graphic method; the A_2 conformation for X = CH_3, Br, NO_2, and the A_2^a conformation for X = OCH_3, formed by rotation about the C(ar)–C(7) bond, appears to be favourable. The same conclusions apply in the case of the substituents X = F, Cl, CN and $N(CH_3)_2$. For para substituted benzoyl isothiocyanates with X = F, CN or $N(CH_3)_2$, the synclinal conformation formed by rotation about the C(7)–N bond, with a dihedral angle τ of about 60°, and the conformation with the superscript *a*, which is formed by rotation about the C(ar)–N bond, are also preferred.

As in the case of para substituted phenyl isocyanates[2], the series of para substituted benzoyl isothiocyanates was used to determine the group dipole moment and angle of the group dipole moment of the –CONCS group (Θ) by means of the optimization condition

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

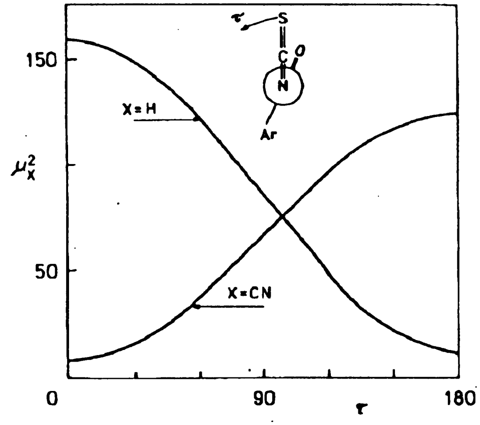


Fig. 1

Dependence of squared dipole moments of benzoyl isothiocyanate and *p*-cyanobenzoyl isothiocyanate on the dihedral angle τ

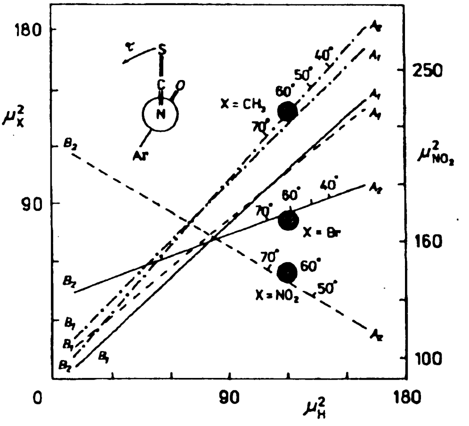


Fig. 2

Graphical comparison of squared dipole moments of meta substituted benzoyl isothiocyanates; *x*-axis: X = H, *y*-axis: X = *m*-CH_3 (dot and dash line), *m*-Br (full line), *m*-NO_2 (dashed line) where $\mu(i)$'s are the experimental dipole moments of selected para substituted benzoyl isothiocyanates and $\mu_a(i)$'s are the corresponding dipole moments determined by vector addition of the group moments. The values obtained are $\mu_{CONCS} = 10.7 \cdot 10^{-30}$ C m and $\Theta = 24°$.

Conclusions concerning the agreement of the experimental dipole moments and those obtained by various quantum chemical methods are difficult to draw[15 - 17]. The agreement is generally poorest for compounds containing hetero atoms[15,16]. This has also been observed by us in the case of heterocumulenes. Tables I and II show that the dipole moments calculated by the MNDO method for meta and para substituted benzoyl isothiocyanates do not agree well with the experimental values. Furthermore, the tables demonstrate that the contributions to the total dipole moment values from the net charges at the sites of the nuclei μ_{chg} differ from the experimental values less than the summary dipole moments μ_{sum} do, and that this situation is still aggravated by the hybrid term μ_{hyb}. It is noteworthy that, with few exceptions, the MNDO calculated dipole moments of the substances investigated follow the same trend as the experimental values, the correlation being linear, viz. $\mu_{exp} = 0.58\ \mu_{sum} + 2.59$ with a correlation coefficient of $r = 0.928$, or $\mu_{exp} = 0.70\ \mu_{chg} + 2.38$, with $r = 0.939$.

It can be concluded that for meta and para substituted benzoyl isothiocyanates, due to the occurrence of the polar –C=O and –NCS bonds, the synclinal conformation ($\tau \approx 60°$) formed by rotation about the C(7)–N bond is preferred to the antiperiplanar conformation. In the meta substituted series, the *A* conformation ($\tau \approx 60°$) is preferred to the *B* conformation (the A^a conformation is prefered to A^b in the case of the substi-

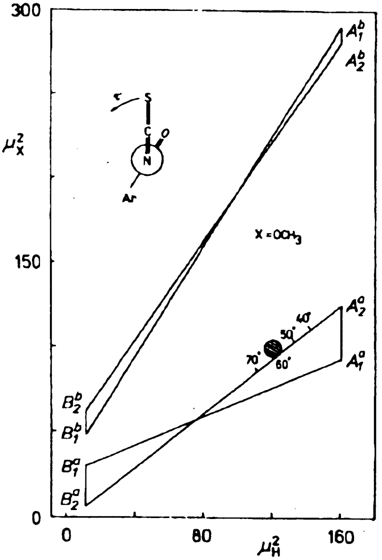


FIG. 3
Graphical comparison of squared dipole moments of *m*-methoxybenzoyl isothiocyanate: *x*-axis: X = H, *y*-axis: X = *m*-OCH$_3$

tuents X = $N(CH_3)_2$ and OCH_3). For para substituted benzoyl isothiocyanates, the *A* conformation ($\tau \approx 60°$) is preferred to *B* (A^b is preferred to A^a for X = OCH_3, ref.[3]). In view of the very low difference between the calculated dipole moments of the above conformations (A^a and A^b) for X = p–$N(CH_3)_2$, viz. $\Delta\mu_a = 0.16 \cdot 10^{-30}$ C m, free rotation of the group seems likely.

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