

REINVESTIGATION OF DIPOLE MOMENTS OF *para* SUBSTITUTED PHENYL ISOCYANATES AND DETERMINATION OF DIPOLE MOMENT OF NCO GROUP BY OPTIMIZATION PROCEDURE

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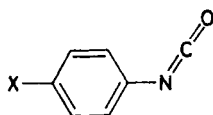
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The values of dipole moments of a series of *p*-substituted phenyl isocyanates have been determined by the method of Halverstadt and Kumler. The experimental dipole moments measured have been used for determination of magnitude and direction of the group dipole moment of NCO group bound to a benzene ring ($7.93 \cdot 10^{-30}$ C m, 21°) by means of a simple optimization procedure.

In the context of complex investigation of physico-chemical properties of heterocumulenes we paid considerable attention¹ also to study of dipole moments of compounds type R—NCY (Y = S, Se). In this present work we have decided to re-investigate the dipole moments of *p*-substituted phenyl isocyanates and to determine the magnitude and direction of the NCO group dipole moment. The dipole moment values of phenyl isocyanate and of some its *p*-substituted derivatives are given in literature^{2,3} but they do not allow any detailed analysis leading to determination of magnitude and direction of the NCO group dipole moment (e.g., various solvents,



X = OCH₃, CH₃, H, F, Cl, Br, CN, NO₂

temperatures, ways of determination). In addition, with respect to the dipole moment values of analogous *p*-substituted phenyl isothiocyanates⁴, the values given for *p*-substituted phenyl isocyanates did not agree with our ideas about substituent effects on dipole moment values. Whereas the dipole moment values decrease in the order from electron-donor to electron-acceptor substituents, the data quoted show just the opposite trend (the value of nitro derivative is distinctly larger than that of the methoxy derivative).

EXPERIMENTAL

The series of *p*-substituted phenyl isocyanates were prepared by the Curtius degradation of azides of corresponding carboxylic acids. The purity of the compounds prepared was checked by comparison with the published⁵ physico-chemical properties.

The values of dipole moments μ were determined according to the method by Halverstadt and Kumler⁶ using Eq. (1) which also involves the correction for atomic polarization a

$$\frac{N_A}{9kT\epsilon_0} \mu^2 = M_2 \left[\frac{3\alpha}{d_1(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \left(\beta + \frac{1}{d_1} \right) \right] - R_D(1 + a). \quad (1)$$

α and β are slopes of the dependences of permittivities and densities on the weight fraction of solute, i.e. $\partial\epsilon_{12}/\partial w_2$, $\partial d_{12}^{-1}/\partial w_2$, the subscripts 1, 2, and 12 denoting solvent, solute, and solution, respectively. The molar refraction R_D was calculated from the atomic increments^{7,8}, and the value of 0.05 was taken for the correction for atomic polarization. The other symbols in Eq. (1) have their usual meanings.

The permittivities and densities of solutions were measured in redistilled and pre-dried (molecular sieves) benzene. The permittivities of solutions were measured with a Dipolmeter DM 01 apparatus with a thermostatted cell DFL 2 (Wissenschaftlich-technische Werkstätten GmbH). The densities of the solutions were determined pycnometrically. The measurements were carried out at the temperature of 293.15 K (20°C). Each concentration dependence of a given compound was determined from 5–7 various concentrations of solutions, the weight fraction values w_2 being varied within the limits from 0.0015 to 0.008.

RESULTS AND DISCUSSION

Table I presents the values of dipole moments of *p*-substituted phenyl isocyanates obtained by the method of Halverstadt and Kumler⁶ as well as the values of overall polarizations $P_{2\infty}$, molar refractions R_D , and slopes of the concentration dependences (α and β). As already stated, the dipole moment values published so far do not allow construction of a consistent series from which it would be possible to determine the magnitude and direction of the NCO group dipole moment. In particular, the dipole moment values for electron acceptor substituents are not available; the value $11.40 \cdot 10^{-30}$ C m given for the nitro derivative seems not to be correct. In fact, the only thoroughly verified dipole moment value is that of the unsubstituted phenyl isocyanate. Various authors give the values about $7.66 \cdot 10^{-30}$ C m for the dipole moment of this derivative ($7.50 \cdot 10^{-30}$ – $7.83 \cdot 10^{-30}$ C m for various solvents, temperatures, and ways of determination), and the value obtained from microwave spectra is $8.07 \cdot 10^{-30}$ C m (ref.⁹). Hence it is impossible to confront our dipole moment values of the series of *p*-substituted phenyl isocyanates with the corresponding values by other authors (except for the unsubstituted phenyl and *p*-methoxyphenyl derivatives). Therefore, we considered it useful to compare our experimental values of dipole moments of *p*-substituted phenyl isocyanates with the respective values calculated by vectorial addition of group dipole moments. This method is currently used for estimation of dipole moments of simple planar molecules where

it gives very good results¹⁰. For most substituents (functional groups) the magnitude and direction of group dipole moments are given in literature^{10,11}. However, no data are available for the NCO group bound to a benzene nucleus. The NCO group dipole moment could be derived from the dipole moment of phenyl isocyanate itself, but the identification of the angle of group dipole moment, C—NCO, with the valence

TABLE I

Dipole moments (μ , 10^{-30} C m) of *p*-substituted phenyl isocyanates ($X-C_6H_4-NCO$) and the respective slope values (α , β) of concentration dependences, overall polarization ($P_{2\infty}$, 10^{-6} m³) and molar refraction (R_D) calculated from the atomic increments^{8,7}

X	α	β	$P_{2\infty}$	R_D^a	μ^b
OCH ₃	6.672	-0.438	217.203	39.854	9.96
CH ₃	6.998	-0.131	214.212	38.074	9.66
H	5.982	-0.322	162.235	33.158	8.26
F	1.468	-0.578	60.572	32.954	3.73
Cl	0.862	-0.346	61.075	38.114	3.36
Br	1.134	-0.687	68.676	40.964	3.70
CN	4.163	-0.581	136.152	38.554	7.16
NO ₂	3.354	-0.631	127.766	39.694	6.79

^a The correction for atomic polarization $a = 0.05$; ^b the published^{2,3,9} values of dipole moments (10^{-30} C m) are for X = OCH₃ 9.93 ($T = 298.15$ K, benzene), X = CH₃ 8.93 ($T = 293.15$ K, benzene), X = H 7.63 ($T = 293.15$ K, benzene), 7.67 ($T = 293.15$ K, benzene), 7.83 ($T = 291.15$ K, benzene), 7.50 ($T = 298.15$ K, tetrachloromethane), 8.07 ($T = 243.15$ K, microwave spectra), X = Cl 2.83 ($T = 298.15$ K, tetrachloromethane), X = NO₂ 11.40 ($T = 298.15$ K, benzene).

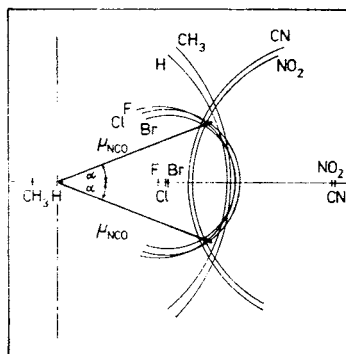


FIG. 1

Determination of the direction of the dipole moment of phenyl isocyanate by the graphical method¹²

angle C—N=C (c. 140°) is not justified and leads to incorrect results when applied in vectorial additions for other *p*-substituted derivatives. For this purpose, a simple graphical method was suggested¹² which can be applied to *p*-substituted benzenes. From Fig. 1 it can be seen that in our case it is impossible to unambiguously estimate the optimum values of magnitude and direction of the NCO group dipole moment by this method. Therefore, instead of the graphical treatment mentioned the magnitude and angle of the NCO group dipole moment was optimized according to the condition:

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

where $\mu(i)$ are the experimentally determined values of dipole moments of selected *p*-substituted phenyl isocyanates, and $\mu_v(i)$ are the corresponding dipole moment values obtained by the vectorial addition of group moments. The results of the optimization according to Eq. (2) are represented in Fig. 1 by the minimum mean distance of all circles, i.e. the optimum values of magnitude ($\mu_{\text{NCO}}^{\text{opt}}$) and direction (Θ^{opt}) of the dipole moment of isocyanate group attached to benzene ring. The values obtained in this way are $\mu_{\text{NCO}}^{\text{opt}} = 7.93 \cdot 10^{-30}$ C m, and $\Theta^{\text{opt}} = 21^\circ$. For comparison let us note that the same treatment applied to dipole moment values of *p*-substituted phenyl isothiocyanates¹ and phenyl isoselenocyanates¹³ leads to the values $\mu_{\text{NCS}}^{\text{opt}} = 10.00 \cdot 10^{-30}$ C m, $\Theta^{\text{opt}} = 13^\circ$; $\mu_{\text{NCS}_e}^{\text{opt}} = 11.57 \cdot 10^{-30}$ C m, $\Theta^{\text{opt}} = 15^\circ$.

The dipole moments of the compounds investigated were also determined by the method of Guggenheim and Smith^{14,15} and the results obtained were compared with the dipole moment values determined according to Halverstadt and Kumler⁶. As such a comparison was carried out earlier¹⁶ with a substantially larger statistical set, let us only mention that in the case of *p*-substituted phenyl isocyanates both the methods give equivalent results.

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