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DIPOLE MOMENTS OF SEPARATED Z- AND E-CONFIGURATED THIOAMIDES

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Abstract: Experimentally determined dipole moments of isolated Z- and E-forms of N-methyl-thioformamide and N-neopentyl-thioformamide show that the Z-configuration is the more stable configuration on account of partial compensation of bond moments, unless steric strain destabilizes this form.

N-alkyl-monosubstituted thioamides occur preferentially in the Z-configuration. In a previous paper 1) evidence has been presented that dipole-dipole interactions can be regarded to cause this effect: experimentally determined dipole moments of Z-configurated thioamides1) (N-methyl-thioformamide: $\mu_{293} = 1.521 \cdot 10^{-29}$ Cm [4.56 D]; N-methyl-thioacetamide: $\mu_{293} = 1.587 \cdot 10^{-29}$ Cm [4.76 D]; N-ethyl-thioacetamide: $\mu_{293} = 1.597 \cdot 10^{-29}$ Cm [4.56 D]; N-propyl-thioacetamide: $\mu_{293} = 2.601 \cdot 10^{-29}$ Cm [4.80 D]; N-butyl-thioacetamide: $\mu_{293} = 1.591 \cdot 10^{-29}$ Cm [4.77 D]), and of thioamides being E-configurated on account of steric influences (N-tert.butyl-thioformamide: $\mu_{293} = 1.724 \cdot 10^{-29}$ Cm [5.17 D]) have supported the assumption that partial compensation of R_1-N and C=S bond-moments (Fig. 1) leads to a lower dipole moment of the Z-configurated molecule which implies that the Z-form is of lower energy thus stabilizing this configuration. But this hypothesis could not yet be supported duly since only experimental dipole moments of differently substituted thioamides were available.

Z-form E-form

Fig. 1

For this reason Z- and E-form of N-methyl-thioformamide and of N-neopentyl-thioformamide have been separated by the chromatographic method described by Walter, Schaumann, and Reubke [2], with the aim of measuring Z- and E-dipole moments of the same compound. It can thus be assumed that in contrast to previously presented results alterations of steric, inductive and mesomeric influences by different substituents can be neglected.

The dipole moments of the Z- and E-form depicted in Fig. 2 were measured at 283 K in benzene solution, i.e. at a temperature which slows down equilibration without freezing of the solvent. The dipole moment of the separated

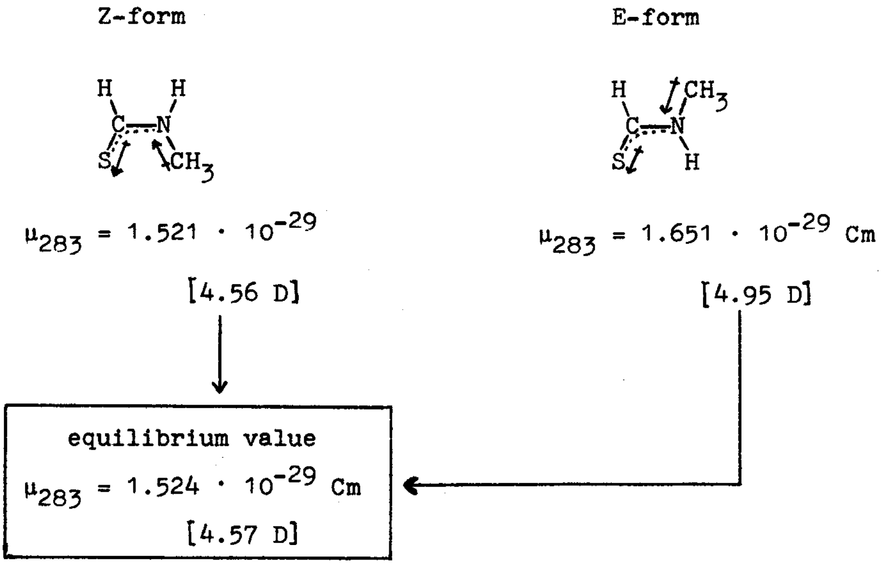

Fig. 2

Z-form μ_{283} = 1.521 · 10^{-29} Cm [4.56 D] is identical with the value obtained earlier at 293 K [1] (μ_{293} = 1.521 · 10^{-29} Cm [4.56 D]) which represents an intermediate value of a Z : E = 88 : 12 mixture [3]. After 5 hours the measurement of the same solution was repeated which now supplied the value of the above mentioned equilibrium mixture of the E- and Z-forms of N-methyl-thioformamide μ_{293} = 1.524 · 10^{-29} Cm [4.57 D].

The dipole moment of the separated E-form of N-methyl-thioformamide proved to be significantly higher (μ_{283} = 1.651 · 10^{-29} Cm [4.95 D]) than that of the Z-form, thus supporting the above described model of partial bond moment compensation. Again, the measurement was repeated after 5 hours, i.e. after equilibrium formation. The equilibrium value obtained by measuring this solution was exactly identical with that of the Z-form solution.

The results of the separated Z- and E-configurated N-neopentyl-thioformamides are shown in Fig. 3. The Z-form has a lower dipole moment (μ_{283} = $1.567 \cdot 10^{-29}$ Cm [4.70 D]) than the E-form (μ_{283} = $1.738 \cdot 10^{-29}$ Cm [5.21 D]). The slight shift to higher values both of the Z- and E-form in comparison to

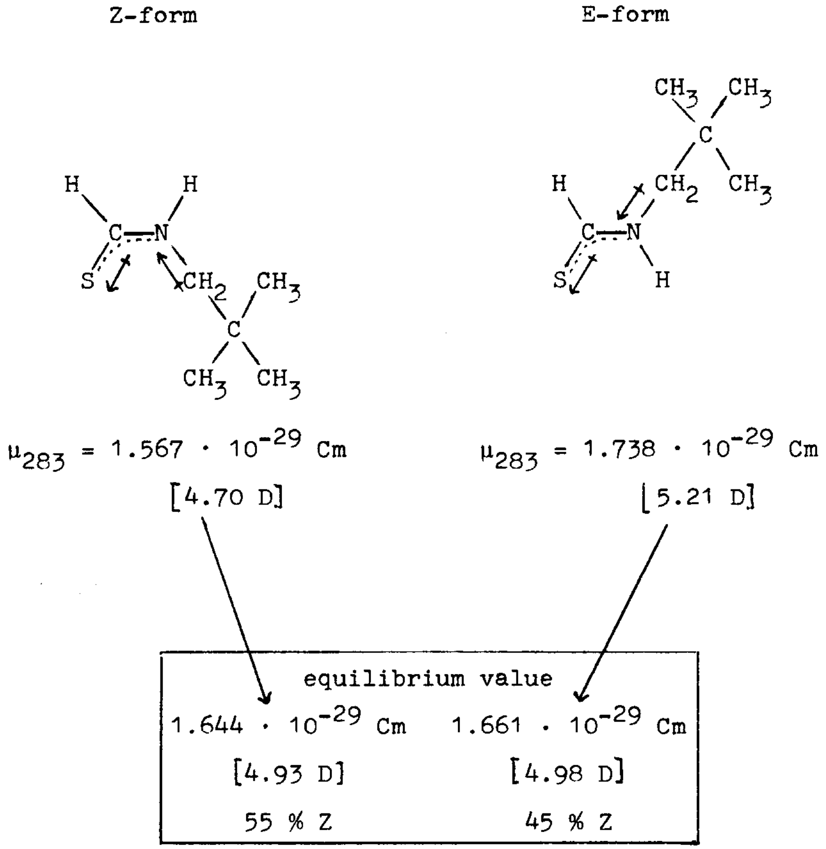

Fig. 3

N-methyl-thioformamide is due to the well known inductive effect within the longer N-alkyl-chain [4], e.g. the dipole moment of the E-configurated N-tert.-butyl-thioformamide (μ_{293} = $1.724 \cdot 10^{-29}$ Cm [5.17 D]) is of the same order of magnitude as that of the separated E-form of N-neopentyl-thioformamide. The equilibrium value obtained after repeating the measurement of the same solutions after 5 hours are $1.644 \cdot 10^{-29}$ Cm [4.93 D] and $1.661 \cdot 10^{-29}$ Cm [4.98 D] resp., which are identical within the limits of this method. The Z : E ratios calculated from these two equilibrium values are Z : E = 55 : 45 and Z : E = 45 : 55, which is in good agreement with the equilibrium value reported by Schaumann [5] who measured by means of NMR-investigations a content of 52.4 ± 0.2 % Z-form in a 10^{-4} mol CCl_4 solution.

It can be concluded from these results that the Z-form is prefered in N-methyl-thioformamide allowing partial compensation of the N-methyl and C=S bond moments, whereas in the case of N-neopentyl-thioformamide the energetically prefered Z-form is less favoured on account of the stronger steric interaction between the N-neopentyl and C=S groups.

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