

# The Torsional Barrier of the Dimethylamino Group in *N,N*-Dimethyltellurobenzamide. A Comparison with *N,N*-Dimethylbenzamide and its Thio and Seleno Analogues

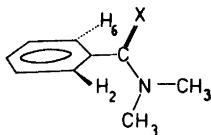
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The torsional barrier of the dimethylamino group in *N,N*-dimethyltellurobenzamide has been determined by variable temperature <sup>1</sup>H NMR spectroscopy. The free energy barrier (80.5 kJ mol<sup>-1</sup>) is slightly lower than in the seleno analogue and thus breaks the trend of increasing barriers for PhCXNMe<sub>2</sub> in the series X=O, S, Se.

The increasing trend is discussed in terms of second order perturbation theory and is related to the bonding parameter for the C=X π bond. The deviation of the telluroamide is ascribed to an increase in the ground state strain due to repulsion between the tellurium atom and the *Z*-*N*-methyl group. This interaction is reflected in an increased shielding of the *E*-*N*-methyl group caused by its deflection into a more strongly shielding region above the aromatic ring.

As *N,N*-dimethyltellurobenzamide (*1d*) has recently become available,<sup>1</sup> it was found of interest to measure the torsional barrier of its dimethylamino group in order to make a comparison with *N,N*-dimethylbenzamide (*1a*), *N,N*-dimethylthio-benzamide (*1b*), and *N,N*-dimethylselenobenzamide (*1c*).



- 1a*, X=O  
*1b*, X=S  
*1c*, X=Se  
*1d*, X=Te

## EXPERIMENTAL

An NMR sample was prepared under nitrogen in degassed *o*-dichlorobenzene (ODC) and sealed under high vacuum. It was possible to record several exchange-broadened <sup>1</sup>H NMR spectra before the sample underwent violent decomposition at ca. 130 °C. Standard complete bandshape analysis of these spectra (all below coalescence), using a singlet signal in the solvent spectrum as a resolution standard,<sup>2</sup> gave a free energy barrier of 80.5 ± 0.5 kJ mol<sup>-1</sup>, fairly independent of the temperature.

The chemical shift values given in Table 1 have been recorded at somewhat different concentrations and temperatures. However, unlike what is found for aliphatic amides and thioamides, the chemical shifts for the *N*-methyl protons in compounds *1a* to *1c* are fairly insensitive to these conditions, and the variations that may occur are too small to affect the conclusions reached in this communication.

The UPS data in Table 2 were recorded with a Perkin Elmer Model PS-18 photoelectron spectrometer, employing the He(I) 21.22 eV resonance line for ionization and the <sup>2</sup>P<sub>3/2</sub> (12.13 eV) line of Xe and the <sup>2</sup>P<sub>3/2</sub> (15.76 eV) line of Ar for calibration.

## DISCUSSION

When comparing this barrier with those of the analogues, it seems advisable to use free energy barriers (Δ*G*<sup>‡</sup>) measured in the same temperature region, rather than activation enthalpies (Δ*H*<sup>‡</sup>), since good Δ*H*<sup>‡</sup> values are not available for all compounds *1*. Besides, these processes can be expected to have activation entropies close to zero.<sup>3</sup>

Table 1. Torsional barriers and  $^1\text{H}$  chemical shifts for the  $\text{Me}_2\text{N}$  groups in *1a* to *1d*.

Compound	X	$\Delta G^\ddagger/\text{kJ mol}^{-1a}$	Temp./K	$\delta_A^b$	$\delta_B$	$\Delta\delta$	Ref.
<i>1a</i>	O	62.3	263	3.005	2.733	0.272	4
<i>1b</i>	S	77.0	365	3.325	2.793	0.532	5
<i>1c</i>	Se	80.8	360	3.433	2.733	0.700	6
<i>1d</i>	Te	80.5	370	3.516	2.568	0.948	This work

<sup>a</sup>Solvent ODC. <sup>b</sup>Downfield from TMS, in slow exchange limit.

The available  $\Delta G^\ddagger$  and chemical shift values are found in Table 1.

The barrier differences between amides and thioamides have previously been discussed in relation to the interaction between the lone pair orbital on the nitrogen atom and the antibonding  $\pi$  orbital ( $\pi^*$ ) in the  $\text{C}=\text{X}$  group.<sup>7</sup> When second order limited basis perturbation theory is employed on the interaction between a filled donor orbital and the lowest empty acceptor orbital (LUMO)\*, the energy of interaction,  $\Delta E$ , which in the present case approximates the torsional barrier, is given by eqn. (1). Here,  $H_{ij}$  is the Hamiltonian matrix element between

$$\Delta E = \frac{2H_{ij}^2}{\Delta\epsilon_{ij}} \quad (1)$$

the interacting orbitals, and  $\Delta\epsilon_{ij} = \epsilon_i - \epsilon_j$  is the difference between their energies. If we assign  $\phi_i$  to the donor orbital and  $\phi_j$  to the acceptor orbital, we obtain eqn. (2) in the CNDO formalism,<sup>8</sup> where  $S_{\text{NC}}$  and  $S_{\text{NX}}$  are the pertinent overlap integrals and

$$H_{ij} = C_{\text{jC}}S_{\text{NC}}\beta_{\text{NC}}^\circ + C_{\text{jX}}S_{\text{NX}}\beta_{\text{NX}}^\circ \quad (2)$$

$C_{\text{jC}}$  and  $C_{\text{jX}}$  are the LCAO coefficients for LUMO of the acceptor.

In Table 1, we find two results, which require explanation, *viz.* the steady increase in  $\Delta G^\ddagger$  in the series *1a* to *1c*, and the drop from *1c* to *1d*.

The first trend can hardly be ascribed to  $H_{ij}$ ,<sup>2</sup> since the first term in eqn. (2) stays constant in the series and the contribution from the second term decreases from *1a* to *1c* ( $\beta_{\text{AB}}^\circ$  is an empirical parameter, the absolute value of which decreases with decreasing electronegativity of A or B<sup>8</sup>). CNDO/2 calculations give much lower energy for the LUMO of CS than of CO, and it seems clear that the observed trend is due to energy gap control rather than to matrix element control.<sup>9</sup> Since the

energy of the donor orbital,  $\epsilon_i$ , is constant, changes in  $\Delta\epsilon_{ij}$  are due to changes in the LUMO energy of the acceptor.

Epiotis *et al.*<sup>10</sup> have shown by simple perturbation analysis that the LUMO energy of a  $\text{C}=\text{X}$  group and the HOMO\*–LUMO energy gap are decreased, when X is chosen from successively lower levels in the same column of the Periodic Table. This is mainly explained by a decrease in the absolute value of the off-diagonal Hamiltonian matrix element in this direction. In the CNDO approximation, this parameter is given by eqn. (3).<sup>8</sup>

$$H_{\text{C}=\text{X}} = \beta_{\text{C}=\text{X}}^\circ S_{\text{C}=\text{X}} \quad (3a)$$

$$\beta_{\text{C}=\text{X}}^\circ = 0.5(\beta_{\text{C}}^\circ + \beta_{\text{X}}^\circ) \quad (3b)$$

Calculation of the overlap integral for the  $\pi$  bond in  $\text{C}=\text{X}$  for  $\text{X}=\text{S}$ , Se and Te, using Slater type orbitals and standard bond lengths gave very similar results ( $S \approx 0.35^{11}$ ). Even if this may partly be due to some deficiency in the second and third row Slater orbitals, it is likely that the effect is mainly due to a diminished absolute value of  $\beta_{\text{X}}^\circ$ .

Ultraviolet photoelectron spectra (UPS) of *1b*–*1d* (Table 2) show three ionization events, 1, 2, and 5, which occur at progressively lower ionization potential (IP) when going down the column. Of these, 1 and 2 are undoubtedly due to either of the lone pair and highest  $\pi$  orbital, but beyond this no safe assignment can be made without a more thorough study. Ionizations 3 and 4 are assigned to  $\pi_3$  and  $\pi_2$  in the benzene ring, respectively, and 5 fits with the expectation for  $\sigma_{\text{CX}}$ . We can thus conclude that the HOMO energy increases in the series  $\text{X}=\text{S}$ , Se, Te, and according to the previous discussion the LUMO energy should decrease in the same succession. Therefore, the observed increase in barrier in the series *1a* to *1c* can be

\* LUMO = lowest unoccupied molecular orbital.

\* HOMO = highest occupied molecular orbital.

Table 2. Vertical IP's (in eV) below 11 eV for PhCXNMe<sub>2</sub>.

X	1	2	3	4	5
S	7.70	8.27	9.26	9.5	10.93
Se	7.33	7.89	9.19	9.4	10.70
Te	6.80	7.50	9.20	9.35	10.5

rationalized by successive lowering of the electronegativity of the atom X in this series. It now remains to be explained why the barrier of *1d* does not fit into the series. A possible rationalization could be that steric strain in the ground state increases in the series *1a* to *1d* due to increasing interaction between the X atom and the Z methyl group. This interaction is probably quite weak in the thioamide, as judged from the *N,N*-diisopropylthioamides described in Ref. 12, where only a weak ground-state strain is found by molecular mechanics calculations. Parameters for similar calculations on seleno- and telluroamides are not available, but use of appropriate van der Waals radii<sup>13</sup> shows that, with unchanged geometry, a considerable interpenetration of the Z-N-methyl group and the X atom must occur in *1c* and even more so in *1d*. The concomitant repulsion must be partly released by an increase in the X=C-N angle, and this in turn leads to an increased twist between the thioamide group and the benzene ring due to stronger interaction with the ortho protons. Also on the side of the X atom, an interaction with the nearest ortho proton will occur. The dihedral angle between the thioamide group and the benzene ring is 63° in *1b*,<sup>14</sup> and an increase in this angle and in the X=C-N angle in *1c* and *1d* is revealed by the chemical shifts of the E-N-methyl protons (Table 1). While the Z-N-methyl is progressively less shielded in the series *1a* to *1d* due to the increasing magnetic anisotropy of the C=X group, the E protons in *1c* and *1d* experience an increase in shielding. This is well explained by the geometric changes discussed above, which move the E protons into successively more shielding regions with respect to the benzene ring.

The ring current effect may in fact be larger than shown by the shift values in Table 1, since in general the E protons appear at 0.2 to 0.5 ppm lower field in thioamides than in amides.<sup>12</sup> This effect, which is ascribed to a larger positive charge on the thiocarbonyl carbon atom, could well progress further in *1c* and *1d* and partly balance the effects of the changes in geometry.

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