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# DIPOLE MOMENTS AND ELECTRONIC STRUCTURE OF 2,6-BIS(DIALKYLAMINO) DERIVATIVES OF 4*H*-PYRAN-4-ONE(THIONE) AND 4*H*-THIOPYRAN-4-ONE(THIONE)

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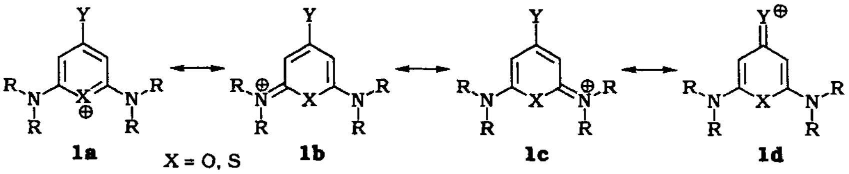
**Dipole moments of a series of 2,6-bis(dimethylamino) and 2,6-bis(pyrrolidino) derivatives of 4*H*-pyran-4-one (2), 4*H*-thiopyran-4-thione (3), 4*H*-pyran-4-thione (4) and 4*H*-thiopyran-4-thione (5) were determined in benzene and dioxane solutions at 25 °C. High values of the dipole moments (6·44–8·44 D) and mesomeric moments originated from delocalization of the nitrogen lone pairs into the π-system of the heterocyclic moieties (1·11–3·08 D) indicate a strong polarization of the molecules 2–5 due to a tendency to stabilize pentamethinium and pyrylium (thiopyrylium) ionic structures. The MNDO-calculated electronic distribution in 2–5 compared with that for the parent 4*H*-pyran(thiopyran)-4-one(thione)s is in line with this conclusion**

It was found that the introduction of powerful electron-releasing substituents into the 2-, 4- and 6-positions of pyrylium and thiopyrylium cations **1** drastically modifies the electron structures and reactivity of these species compared with the unsubstituted cations.[1–8] The changes in reactivity of 2,4,6-tris(dialkylamino)-pyrylium salts and their thio analogues are of such an extent that these compounds become susceptible to electrophilic, rather than nucleophilic, substitution reactions (nitration and Friedel–Crafts-type reactions) under very mild conditions. This chemical behaviour implies a compensation of π-deficiency of the cationic ring system due to polarization that may be described by the resonance of several polar structures ($Y = NR_2$).

The same kind of polarization is characteristic of recently synthesized 2,6-bis(dialkylamino)-4*H*-pyran-4-ones (**2**), 4*H*-thiopyran-4-ones (**3**), 4*H*-pyran-4-thiones (**4**) and 4*H*-thiopyran-4-thiones (**5**),[3] which may be viewed as electroneutral analogues of **1** in which $Y = O^-$ or $S^-$.

Compounds **2**–**5** bearing in the 2- and 6-positions dimethylamino or pyrrolidino groups, respectively, display significantly enhanced basicity (*ca* 6 pH units higher than their analogues not containing



Formula 1

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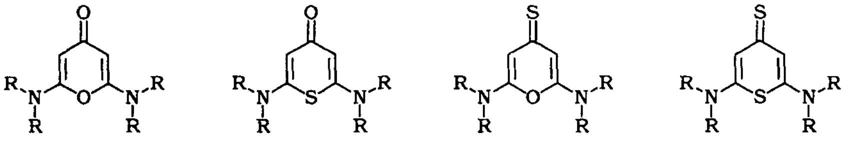


**2** **3** **4** **5**

Formula 2

dialkylamino substituents in the 2- and 6-positions)[3] and increased energy barriers to the C—N rotations,[5] both effects being caused by a contribution of the type **1a–c** (Y = O$^-$, S$^-$) polar structures. The electroneutrality of **2–5** allows us, as distinct from bis(alkylamino)- (**1**, Y = H, R) and tris(alkylamino)pyrylium and -thiopyrylium salts (**1**, Y = NAlk$_2$), to apply the dipole moment measurement technique in order to determine the degree of polarization of their molecules, the structures of which represent two-sided vinylogous ureas and thioureas bonded by the heteroatoms.

The dipole moments were determined in benzene and/or dioxane solutions at 25 °C using the heterodyne method for the measurement of dielectric permittivities. The dielectric permittivities of 4–5 solutions were measured starting from the saturated solutions at ambient temperature and ending with 15–20-fold diluted solutions. Since a linear dependence between dielectric permittivities (and densities) of solutions and concentrations is necessary (by the equation applied) and does in fact exist, it is not important to report exact values. The correction for atomic polarization was used as 5% of the molecular refraction. The Hedestrand equation[9] was employed for the extrapolation of the polarization to infinite dilution and the electronic polarization was calculated as a sum of bond refractions. The data thus obtained are given in Table 1.

High values of dipole moments of bis(dialkylamino)-4*H*-pyran-4-one (thione)s and -4*H*-thiopyran-4-one-(thione)s clearly indicate a very strong polarization resulting from tendency to stabilize the ionic pentamethinium (**1b** and **c**) and pyrylium (thiopyrylium) structures (**1a**). To evaluate the extent of this polarization the experimental dipole moments of bis(dimethyl-

Table 1. Molar polarization ($P_\infty$), electronic polarizations ($P_{el}$) and dipole moments [$\mu = 0{\cdot}221(P_\infty - 1{\cdot}1P_{el})^{1/2}$] of type 2–5 compounds

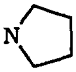
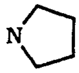
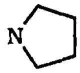
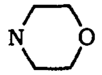
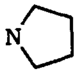
| Structural type | 2,6-Dialkylamino group | M.p. (°C) | Solvent | $P_\infty$ (cm$^3$) | $P_{el}$ (cm$^3$) | $\mu$ (D) |
|---|---|---|---|---|---|---|
| 2 | NMe$_2$ | 159–160·5 | Dioxane | 1095 | 53·9 | 7·11 |
| |  | 175–176·5 | Benzene | 1327 | 68·4 | 7·82 |
| | | | Dioxane | 1324 | 68·4 | 7·81 |
| 3 | NMe$_2$ | 194–195 | Benzene | 910 | 56·5 | 6·44 |
| | | | Dioxane | 987 | 56·5 | 6·72 |
| |  | 208–210 (decomp.) | Dioxane | 1150 | 71·0 | 7·23 |
| 4 | NMe$_2$ | 230 (decomp.) | Benzene | 1561 | 62·6 | 8·53 |
| | | | Dioxane | 1668 | 62·6 | 8·84 |
| |  | 250–253 (decomp.) | Benzene | 1678 | 77·3 | 8·82 |
| |  | 275–276 (decomp.) | Dioxane | 1341 | 76·8 | 7·80 |
| 5 | NMe$_2$ | 234–235 (decomp.) | Benzene | 1286 | 65·7 | 7·70 |
| | | 210–212 (decomp.) | Benzene | 1609 | 79·9 | 8·62 |
| |  | | Dioxane | 1588 | 79·9 | 8·56 |

Table 2. Comparison of additive and experimental dipole moment values of bis(dimethylamino) derivatives of compounds **2**–**5**

| Structure | $\mu_{add.}$(D)[a] | $\mu_{exp.}$(D) | $\mu = \mu_{exp.} - \mu_{add.}$(D)[b] |
|---|---|---|---|
| **2** | 5·09 | 7·11 | 2·02 |
| **3** | 5·33 | 6·44 | 1·11 |
| **4** | 5·45 | 8·53 | 3·08 |
| **5** | 5·78 | 7·70 | 1·92 |

[a] The following values for the parent heterocyclics were used:[10] 4*H*-pyran-4-one, 3·72 D; 4*H*-thiopyran-4-one, 3·96 D; 4*H*-pyran-4-thione, 4·08 D; 4*H*-thiopyran-4-thione, 4·41 D. The dipole moment of the dimethylamino group is taken to be equal to 1·58 D and the angle $\theta = 30°$.

[b] Owing to $C_{2v}$ symmetry of all the compounds, the dipole moment vectors direct along the X—C-4 axis. The effect of non-polarity of the dialkylamino groups is negligible compared with the calculated mesomeric effects. Moreover, MNDO calculations with the full geometry optimization we described indicate planarity of the dimethylamino groups. No free rotation about the C—N bond occurs, as also follows from NMR studies.[5]

amino) derivatives of **2**–**5** are compared in Table 2 with the values calculated by the vector addition scheme of moments of polar fragments and groups, i.e. unsubstituted 4*H*-pyran-4-one(thione), 4*H*-thiopyran-4-one(thione) and dimethylamino groups. The additive values thus calculated imply, obviously, an absence of mesomeric interaction between the chosen molecular fragments. Therefore, the difference ($\Delta\mu$) between the vectors of experimental and additive dipole moments is a characteristic of the above interaction.

As can be seen from the $\Delta\mu$ values in Table 2, the mesomeric interaction effected by the inclusion of two 2,6-positioned dialkylamino groups in the $\pi$-system of **2**–**5** is fairly large. This conclusion stems from a comparison of $\Delta\mu$ values with mesomeric moments in the benzene ring, evaluating the degree of $\pi$-delocalization between electron-donating and electron-withdrawing groups in a *para* position.[11] In the case of *p*-dimethylaminonitrobenzene and *p*-dimethylaminobenzaldehyde, the mesomeric moments are equal to 1·48 and 1·53 D, respectively. It is worth noting that mesomeric moments of $\Delta\mu$ arising from the interaction of $\pi$-systems of dimethylamino groups with 4*H*-pyran-4-one(thione) systems (**2** and **4**) are approximately 1 D larger than those with 4*H*-thiopyran-4-one(thione) ones.

This may be well understood from the perturbation MO theory point of view, accounting for the fact that according to MNDO calculations[12] C-2 centres in 4*H*-pyran-4-one(thione) are positively charged (Scheme 1). In both heterocyclic systems C-2 centres aquire large positive charges on introduction of dimethylamino groups into the 2,6-positions.

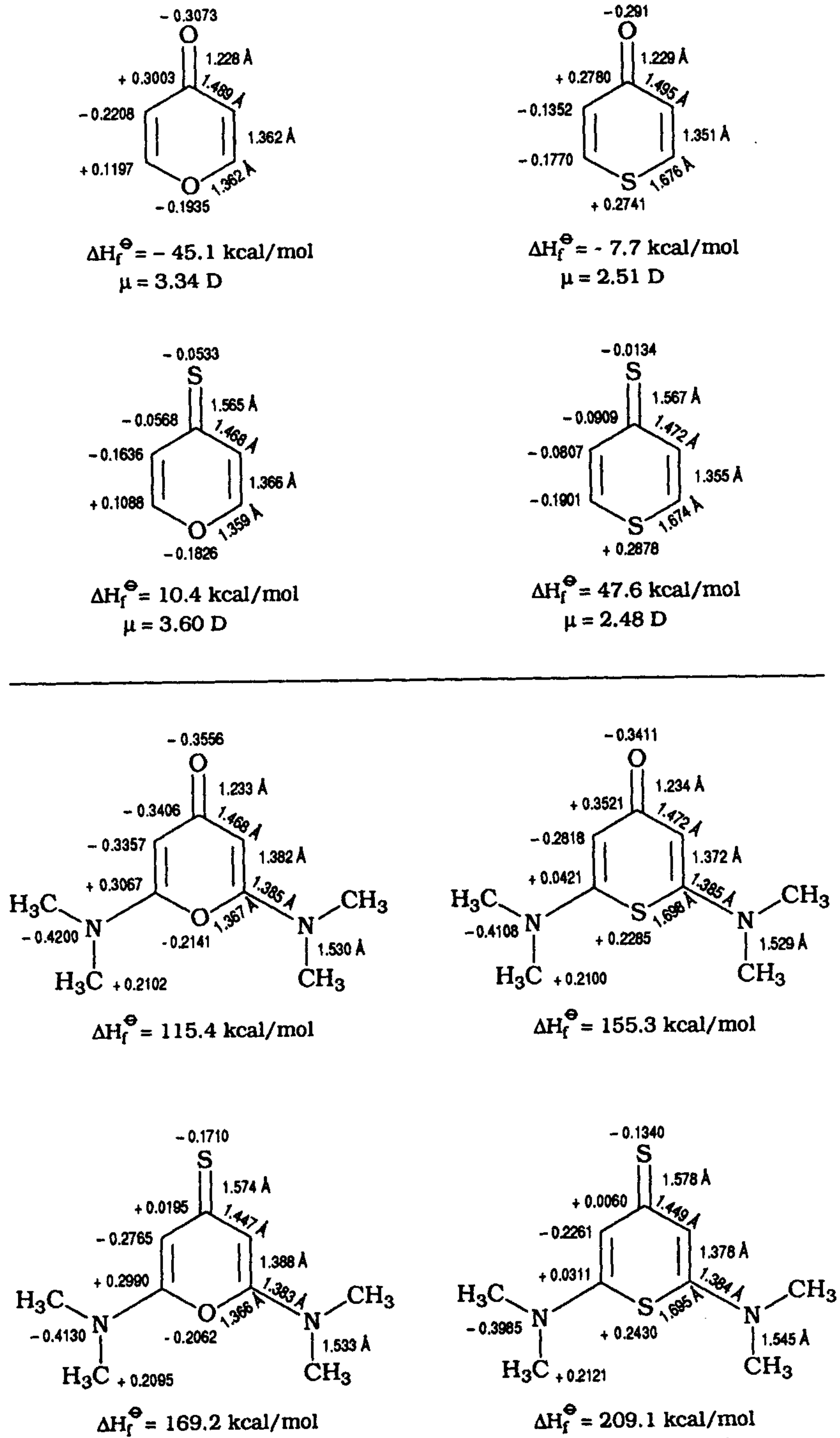
MNDO-calculated values of the dipole moments of the 2,6-bis(dimethylamino) derivatives **2**–**5** (Table 3) are in reasonable agreement with the experimental values. From the charges $\Delta q(3)$ accumulated at C-3 atoms of 4*H*-pyran-4-one(thione) and 4*H*-thiopyran-4-one(thione) systems on dimethylamino substitution in the 2,6-positions, the trend may be traced to the formation of a charge-alternated pentamethinium system, in addition to facilitating electrophilic attack at the 3,5-positions. The $\Delta q(=\text{S})$ values (**4** and **5**) are significantly larger than the $\Delta q(=\text{O})$ ones (**2** and **3**), which indicates a larger contribution of the pyrylium and thiopyrylium resonance forms of type **1a** in the case of thiones **4** and **5** than for their cyclic ketone analogues **2** and **3**.

As can be seen from the data in Table 1, the dipole moments of the 2,6-bis(pyrrolidino) derivatives **2**–**5** are in each case larger than those of the 2,6-bis(dimethylamino) derivatives, which indicates higher polarization and, therefore, a larger contribution of the zwitterionic resonance forms **1a**–**c** and greater double-bond character of the C-2—N and C-6—N bonds in the former compounds. This finding is in line with the observation of a significant lowering of the rotational barriers about the C—N bonds on replacement of the pyrrolidino substituent in **2** and **3** by dimethylamino groups.[5]

Table 3. MNDO-calculated heats of formation ($\Delta H_f^{\ominus}$), dipole moments, charges at C-3 $q(3)$ of exocyclic oxygen $q(=\text{O})$ or sulphur $q(=\text{S})$ atoms for 2,6-bis(dimethylamino) derivatives **2**–**5** and differences between these and charges at the respective positions in 2,6-unsubstituted 4*H*-pyran-4-one(thione) and 4*H*-thiopyran-4-one(thione).

| Structure | $\Delta H_f^{\ominus}$ (kcal mol$^{-1}$) | $\mu$(D) | $q(3)$ | $\Delta q(3)$ | $q(=\text{O, S})$ | $\Delta q(=\text{O, S})$ |
|---|---|---|---|---|---|---|
| **2** | 115·4 | 7·21 | −0·336 | −0·115 | −0·356 | −0·049 |
| **3** | 155·3 | 6·10 | −0·282 | −0·147 | −0·341 | −0·050 |
| **4** | 169·2 | 8·39 | −0·277 | −0·113 | −0·171 | −0·116 |
| **5** | 209·1 | 6·94 | −0·226 | −0·145 | −0·134 | −0·121 |

[a] 1 kcal = 4·184 kJ.



Scheme 1. MNDO calculations (full geometry optimization)

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