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A DIPOLE MOMENT STUDY OF *N*-METHYL AND *N*,*N*'-DIMETHYL-IMIDAZOLIDIN-2-ONES, IMIDAZOLIDINE-2-THIONES AND -2-SELENONES

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ABSTRACT

The electric dipole moments in benzene and dioxan of potentially tautomerizable *N*-methylimidazolidin-2-one, *N*-methylimidazolidine-2-thione and -2-selenone clearly support the lactam structure for these compounds. The fact that their dipole moments in dioxan are markedly greater than those in benzene is explained by a higher (HN—C=Y) mesomeric moment in the hydrogen-bonded solute · · · dioxan complexes. Analysis of the dipole moments in benzene of *N*,*N*'-dimethylimidazolidin-2-one, *N*,*N*'-dimethylimidazolidine-2-thione and -2-selenone shows that the mesomeric moment (due to contribution of \dot{N} =C— \bar{Y} zwitterionic valence structures) gradually increases on going from Y = O to Y = S, and Y = Se. Finally, preferred conformations, from their dipole moments in benzene, are suggested for tetramethylurea and tetramethylthiourea.

INTRODUCTION

During the last decade a number of physico-chemical studies have been carried out on imidazolidin-2-one, imidazolidine-2-thione and -2-selenone and their N-methyl and N,N'-dialkyl substituted derivatives [1--6], by using far-IR spectroscopy [1], He(I) and X-ray photoelectron spectroscopy [2, 3]. Also determined were the self-association constants of the N-methyl derivatives [4, 5], and the stability constants of the adducts formed between various imidazolidine-2-thiones and -2-selenones and molecular iodine [6]. Although dipole moment studies have been reported for N,N'-dimethylimidazolidin-2one and N,N'-dimethylimidazolidine-2-thione [7, 8], it seemed necessary to re-examine the dipole moments of these compounds because of conflicting results for the values of the dipole moment in benzene (μ_b) and dioxan (μ_d)

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of N,N'-dimethylimidazolidin-2-one ($\mu_b = 4.05 \text{ D}$, $\mu_d = 4.09 \text{ D}$ [7], and $\mu_b = 2.58 \text{ D}$, $\mu_d = 2.64 \text{ D}$ [8])*.

In the present work, the electric dipole moments of potentially tautomerizable N-methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone $(I_a, I_b \text{ and } I_c)$, N,N'-dimethylimidazolidin-2-one, N,N'-dimethylimidazolidine-2-thione and -2-selenone $(II_a, II_b \text{ and } II_c)^{**}$ were measured in benzene and dioxan or in benzene at 30.0°C (see Fig. 1). Using the results obtained, the possibility of lactim—lactam tautomerism was investigated for the N-methyl derivatives, and the mesomeric moments were calculated for all the ureas studied. Preferred conformations in benzene for non-planar tetramethylurea and tetramethylthiourea, from their known dipole moments [9], are also discussed in the light of our results on N,N'-dimethylimidazolidin-2-one and N,N'-dimethylimidazolidine-2-thione.

DISCUSSION

Lactam—lactim tautomerism in N-methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone

Unlike N,N'-dimethylimidazolidin-2-one, N,N'-dimethylimidazolidine-2thione and -2-selenone (II), which exist as lactams, N-methylimidazolidin-2one, N-methylimidazolidine-2-thione and -2-selenone enolize to give the lactim tautomers which can exist in two planar conformations I' and I" (Fig. 2).

Clearly the electric dipole moments in benzene and dioxan, given in Fig. 1, of I_a , I_b and I_c (Y = O, S or Se) support the lactam configuration for these



$$\begin{split} \mathbf{I}_{a} & (\texttt{Y}=\texttt{O}, \ \texttt{R}=\texttt{Me}, \ \texttt{R}'=\texttt{H}): \mu_{b}=3.72 \ \texttt{D} \ (\texttt{B}), \ \mu_{d}=3.91 \ \texttt{D} \\ \mathbf{I}_{b} & (\texttt{Y}=\texttt{S}, \ \texttt{R}=\texttt{Me}, \ \texttt{R}'=\texttt{H}): \mu_{b}=4.82 \ \texttt{D}, \ \mu_{d}=5.47 \ \texttt{D} \\ \mathbf{I}_{c} & (\texttt{Y}=\texttt{Se}, \ \texttt{R}=\texttt{Me}, \ \texttt{R}'=\texttt{H}): \mu_{b}=5.28 \ \texttt{D}, \ \mu_{d}=5.89 \ \texttt{D} \end{split}$$

 $\begin{aligned} &\Pi_{c} (Y = 0, R = R' = Me) : \mu_{b} = 4.08 \text{ D} \\ &\Pi_{b} (Y = S, R = R' = Me) : \mu_{b} = 5.20 \text{ D} \\ &\Pi_{c} (Y = Se, R = R' = Me) : \mu_{b} = 5.66 \text{ D} \end{aligned}$

Fig. 1. N-Methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone (as lactams), and N,N'-dimethylimidazolidin-2-one, N,N'-dimethylimidazoline-2-thione and -2-selenone.

^{*1} Debye (D) = 3.336×10^{-30} Cm. In our opinion, the Debye unit is better suited to molecular structures than the coulomb meter which has too high a magnitude. **Also called N,N'-dimethylethyleneurea and N,N'-dimethylethylenethiourea [7], 1,3-dimethylimidazolin-2(3H)-one and 1,3-dimethylimidazolin-2(3H)-thione [8].



Fig. 2. Lactam and lactim tautomers of N-methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone, and the methylated analogues condensed with a benzene ring.

compounds since: (i) The observed values are close to the dipole moments measured in benzene of N,N'-dimethylimidazolidin-2-one, N,N'-dimethylimidazolidine-2-thione and -2-selenone (II_a , II_b and II_c); the dipole moments in benzene and dioxan of pyrrolidine-2-one (3.55 [10], and 3.79 D [11] or 3.80 D [12]) are of the same order of magnitude as those in benzene and cyclohexane of N-methylpyrrolidin-2-one, 4.09 [13] and 3.75 D [14]. (ii) For the lactim tautomers of I, conformers I" can be discarded because of (Me, H) steric interference and electrostatic repulsion between the C-Y-H and C=N'-C dipoles. Conformers I' benefit from (H,N') attraction and a favourable electrostatic potential between the Me-N and C-Y-H dipoles (see Fig. 2); like methyl formate [15], O-methyl imidates (existing in the E configuration) are in an antiperiplanar conformation [16]. Calculation of the dipole moments of I' models by using an additive vector scheme is made difficult here because of interaction between the (N-C=N) and (Y-C=N)mesomeric moments whose values cannot be equated to those in more simple compounds, such as 1,5-diazabicyclo[4.4.0] non-5-ene [17], 1-methoxybutyrolactim [18] or 2-ethyl-2-thiazoline [19, 20]. However, approximate values for the dipole moments of lactim tautomers (as I') of imidazolidin-2-one and imidazolidine-2-thione can be obtained from the known dipole moments in benzene or dioxan [8] of N-methyl-2-methoxybenzimidazole (2.80 and 2.91 D) and N-methyl-2-methylthio-2-benzimidazole (2.51 and 2.58 D) which, principally, differ from the former by existence of a (N-Ph) mesomeric moment m_p (see Fig. 2). Comparison of the dipole moments in benzene of N,N'-dimethylbenzimidazole-2-thione (4.04 D [8]) and N,N'-dimethylimidazolidine-2-thione (5.20 D) affords for m_p a value of

 $m_{\rm p} = (5.20 - 4.04)/\sqrt{3} = 0.67 \text{ D*}$. Taking this value of $m_{\rm p}$, and substituting Me-Y for H-Y yields $\mu(I'_{\rm a}) \sim 2.3 \text{ D}$ and $\mu(I'_{\rm b}) \sim 2.0 \text{ D}$, to be compared with the experimental moments in benzene and dioxan of the compounds, $\mu(I_{\rm a}) = 3.72$ [8] and 3.91 D, $\mu(I_{\rm b}) = 4.82$ and 5.47 D, respectively.

Further, the IR spectra of N-methylimidazolidine-2-thione and -2-selenone in dichloromethane and carbon tetrachloride do not contain any bands ascribable to H—S or H—Se bonds. Analogous imidazol-2-one and imidazole-2-thione have been shown to exist in the lactam configuration [21].

Since the classical valence structures of lactam and lactim tautomers of N-methylimidazolidin-2-one and N-methylimidazolidine-2-thione have approximately equal energies, these being (in kJ mol⁻¹) 4763.1 and 4762.6, 4599.9 and 4602.8, calculated from Pauling's covalent bond-energy increments [22], HN'

the results show that conjugation energy for the C=Y groups is higher MeN

than the sum of the conjugation energies of interacting MeN–C=N' and HY-C=N' groups.

The effect of dioxan on the dipole moments of N-methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone

A marked increase in the dipole moments of N-methylimidazolidin-2one, N-methylimidazolidine-2-thione and -2-selenone is observed on going from benzene (3.72 [8], 4.82 and 5.28 D) to dioxan as solvent (3.91, 5.47 and 5.89 D), $\Delta \mu = 0.19$, 0.65 or 0.61 D.

It has been shown that the dipole moments in dioxan, and also in benzene, nearly correspond to those of the hydrogen-bonded complexes between the free solute and weakly basic solvent [23, 24]. The effect of benzene on the dipole moment could not be determined since the compounds were insufficiently soluble in an unactive solvent such as cyclohexane, but it can be inferred that it is small with respect to that of dioxan. Accordingly the $\Delta \mu_d$ values were equated to the $\Delta \mu$ values. By so doing, the directions of I (I_a, I_b or I_c) in benzene can be calculated by solving the appropriate vectorial equation

$$\mu(\mathbf{I}) = \mu(\mathbf{II}) + [\mu(\mathbf{H}-\mathbf{N}) - \mu(\mathbf{M}\mathbf{e}-\mathbf{N})] \cdot \mathbf{u} + \Delta \mathbf{m}$$

 $= \mu(II) + (1.25 - 0.86) \cdot u + \Delta m$

where u denotes a unit vector along the H—N bond axis, 1.25 and 0.86 D are calculated from the dipole moments in benzene of ammonia and trimethylamine (1.41 and 0.86 D [25]), and Δm is the change in the (RN'—C=Y)

^{*}Cumper and Pickering's figures for the dipole moment of N,N'-dimethylbenzimidazol-2one in benzene and dioxan (2.49 and 2.51 D [8]) were not used in calculating m_p, since we could not confirm their value for N,N'-imidazolidin-2-one in benzene (see Table 1); taking our value for the latter (4.08 D), gives $m_p = 0.91$ D.

mesomeric moment when one methyl group (in II) is replaced by one hydrogen atom to give the N-methyl derivative I. The Δm values are only -0.31, -0.32 and -0.31 D in I_a, I_b and I_c, respectively, and the angles that the gross dipole moments of I_a, I_b and I_c make with the CNC bisector are 4.0, 3.5 and 2.5° (Fig. 3).

Hydrogen bonds A—H···B do possess an intrinsic polarity $\Delta \mu$ as a result of their hybrid character [26]*, A—H···B \leftrightarrow A⁻H—B⁺. This gives rise to a $\Delta \mu_h$ term directed along the H—A bond axis, from B towards A. In the complexes of the N-methyl ureas with dioxan the additional σ charge, related to the $\Delta \mu_h$ dipole, must effect an increase (Δm_d) in the (HN'—C=Y) mesomeric moment, by lowering the electronegativity of nitrogen.

The observation that the $\Delta \mu_d$ values for I_a , I_b and I_c are all positive (0.19, 0.65 and 0.61 D) is of great interest since ignoring the Δm_d term, that is equating $\Delta \mu_d$ to $\Delta \mu_h$, lowers the dipole moment on passing from benzene to dioxan, contrary to experiment. As a consequence, not only the Δm_d vectors exist, but they play a major role in rationalizing the dipole moments in dioxan of these weakly acidic compounds.

In the complexes with dioxan of N-methylacetamide and N-methylthiopropionamide, both existing in the Z configuration [27], the $\Delta \mu_h$ and Δm_d vectors almost act in the same direction and, therefore, the $\Delta \mu_h$ terms are smaller than those observed for $\Delta \mu_d$. From the known dipole moments of these Nmethyl amides in benzene (3.85 and 4.44 D) and dioxan (3.97 and 4.91 D) [28], one derives $\Delta \mu_h < 0.12$ D and $\Delta \mu_h < 0.47$ D respectively. Taking $\Delta \mu_h$ as 0.15, 0.4 and 0.4 D in the complexes with dioxan of N-methylimidazolidin-2-one, N-methylimidazolidine-2-thione and -2-selenone, respectively, calculation gives $\Delta m_d = 0.2$, 0.7 and 0.7 D; these values, as expected, parallel the mesomeric moments in benzene of N,N'-dimethylimidazolin-2-one, N,N'-dimethylimidazolidine-2-thione and -2-selenone (1.59, 3.40 and 3.90 D), and those (also in benzene) of N,N-dimethylacetamide, N,N-dimethyl-



 $I_a: N-methylimidazolidin-2-one$ $I_a: N_i N'-dimethylimidazolidin-2-one$

Fig. 3. Constructing the dipole moments in benzene (IB) and in dioxan (ID) of N-methylimidazolin-2-one, starting from that in benzene (IA) of N,N'-dimethylimidazolidin-2-one. Point I lies 22.0 cm from point A.

*Not A—H · · · B ↔ A⁻ H—B, as inadvertently written in ref. 23 on p. 251.

thioacetamide and N,N-dimethylselenoacetamide (1.25, 2.75 and 3.10 D), calculated as shown later.

Mesomeric moments in N,N'-dimethylimidazolidin-2-one, N,N'-dimethylimidazolidine-2-thione and -2-selenone

These ureas $(II_a, II_b \text{ and } II_c)$ are resonance hybrids of a covalent structure C and two equally contributing zwitterionic structures Z' and Z" (Fig. 4). The mesomeric moments $(M = M_a, M_b \text{ or } M_c)$ can be calculated from the equation $M = \mu(II) - \mu(C)$, where $\mu(C)$ is the so-called primary moment of the molecule.

For N,N'-dimethylimidazolidin-2-one, $\mu_a(C)$ can be equated to $\mu(H_2C=O)$ + $\mu(cyclopentanone) - \mu(acetone)$ since: (i) the molecule, like the ureas

[29], can be regarded as planar and, consequently, $\mu \begin{pmatrix} Me \\ C-N \\ Me \end{pmatrix} = 2 \mu (Me)$

× cos 60° = $\mu(H-C_{sp^3}) - \mu(H-C_{sp^2})$; (ii) the carbonyl dipole gives rise to induction dipoles (through space) in the methylene groups but there are not, as in cyclopentanone, CH₂-C=O hyperconjugation mesomeric moments*. Taking $\mu(H_2C=O) = 2.34$ D in the gaseous phase [30], μ (cyclopentanone) = 2.93 D [31] and μ (acetone) = 2.78 D [32], both in benzene, we obtain $\mu_a(C) = 2.49$ D, and $M_a = 4.08 - 2.49 = 1.59$ D.

For the sulphur analogue (II_b), only the dipole moments of thioformaldehyde and propanethione were measured (1.65 D in the gaseous phase [33] and 2.37 D in benzene [34], respectively). Assuming $\mu_b(C) = 1.65 + (2.93 - 2.78) = 1.80$ D, leads to $M_b = 5.20 - 1.80 = 3.40$ D.

Since the dipole moment of linear S=C=Se is very small (0.031 D [35]), and those of OCS and OCSe (O=C=Y) are almost the same (0.72 [36] and 0.754 D [37]), it can be inferred that $\mu_c(C) = \mu_b(C) - 0.03 = 1.77$ D; accordingly, M_c is 5.66 - 1.77 = 3.89 D in N,N'-dimethylimidazolidine-2-selenone.



Fig. 4. Covalent and zwitterionic valence structures for ureas (Y = 0, S or Se).

^{*}In this approximate treatment, there is no need to take into account the fact that $\mu(H-C_{sp^2})$ is slightly higher than $\mu(H-C_{sp^3})$, by 0.2 D say. A correction for the solvent (benzene) effect on the gas moments of formaldehyde and thioformaldehyde can also be neglected here.

For symmetrical unless, the total contribution of zwitterionic structures $(x = x_a, x_b \text{ or } x_c \text{ for } Y = O, S \text{ or Se})$ can be obtained from the relationships (see Fig. 4)

$$\mu = (1 - x) \cdot \mu(C) + (x/2) \cdot \mu_{y}(Z') + (x/2) \cdot \mu_{y}(Z'')$$
$$M = \mu - \mu(C) = x \cdot [\mu(Z) - \mu(C)]$$

where

$$\mu(Z) = [\mu_{y}(Z') + \mu_{y}(Z'')]/2$$

 $M = x \cdot \{ [\mu(C-Y) - \mu(C=Y)] - [\mu(C=N) - \mu(C-N)] \cdot \cos(NCN/2) + e \times L \}$

with $\mu(C-Y) - \mu(C=Y) = \mu(Me-Y) - \mu(H_2C=Y) = 1.1 - 2.34, 1.2 - 1.65$ and 1.1 - 1.6 for Y = O, S or Se, $\mu(C=N) - \mu(C-N) = \mu(H_2C=N) - \mu(Me-N)$ = 1.76 - 0.86, NCN = 110° (as in ethylenethiourea [29]), $e = 4.80.10^{-10}$ c.g.s.e.s., and L (the actual distance between the mid-point of N' ··· N" and the Y nucleus) is 2.00, 2.47 and 2.62 ± 0.05 Å [29]*. If so, calculation gives $x_a = 0.20, x_b = 0.31$ and $x_c = 0.34$.

Such an increase in the x value on going from N,N'-dimethylimidazolidin-2-one to N,N'-dimethylimidazolidine-2-thione, and to N,N'-dimethylimidazolidine-2-selenone, is in accord with the low-frequency vibrations of the C=S and C=Se bonds [1], and with their He(I) photoelectron spectra giving the N1s, S2p and Se3p_{3/2} energies [3]. This order for the mesomeric effect is also indicated by the self-association constants of N-methylimidazolidin-2one, N-methylimidazolidine-2-thione and -2-selenone [4, 5], and by the stability constants of the adducts formed between N,N'-dimethylimidazolidine-2-thione and -2-selenone and molecular iodine [6].

The mesomeric moments of each N—C=Y group calculated from the M values given above (1.59, 3.40 and 3.90 D) are $m_a = 0.89$ D, $m_b = 1.83$ D and $m_c = 2.08$ D in II_a, II_b and II_c, respectively. They can be compared to the mesomeric moments (designated by m^*) of N,N-dimethylacetamide, N,N-dimethylthioacetamide and N,N-dimethylselenoacetamide, whose dipole moments in benzene are 3.81 [38], 4.77 [39] and 5.10 D [17]. Assuming that $m^* = \mu$ [MeC(=Y)NMe₂] — μ (MeCH=Y) and that the m* vector is directed along the N···Y line (as theoretically indicated by zwitterionic structures)*, and taking μ (MeCH=O) = 2.75 D [42], μ (MeCH=S) = 2.33 D [43]

^{*}This can be justified as follows. Calculation of the dipole moment of gaseous formamide (3.714 D [40]), from $\mu(H_2C=O) = 2.34$ D [30], $\mu(H_2N) - \mu(Me_2N) = 1.25 - 0.86 = 0.39$ D (p. 242), and putting the m* vector (adjusted to be 1.18 D) along the N…O line, leads to a vector that makes an angle of 42.0° with the N—C bond axis, which is in accord with the angle (39.5°) indicated by microwave spectroscopy [40]. Arguments put forward by Exner and Papouskova [41], from analysis of the dipole moment of N.N-dimethylbenz-amide, suggesting the m* vector to be directed along the N—C bond axis are not convincing because of complexity of the molecule, which contains two mesomeric moments [m*(N—C=O) and m(Ph—C=O)] which are not independent of each other.

and μ (MeCH=Se) = 2.30 D (assumed), calculation gives $m_a^* = 1.25$ D, $m_b^* = 2.75$ D and $m_c^* = 3.10$, respectively. Competition between mesomeric effects of the two N—C=Y groups in the ureas explains why the *m* value is much lower than the corresponding m^* figure. The values of the ΔG barriers to rotation for the dimethylamino group are (in kJ mol⁻¹) 44.5 only in *N*,*N*-dimethylurea [44], 88.0 and 79.5 in *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, respectively, [45], 57.2 in *N*,*N*-dimethylthiourea [46] but 110.9 and 90.4 in *N*,*N*-dimethylthioformamide and *N*,*N*-dimethylthioacetamide [45], while the ΔG value is 95.4 in *N*,*N*-dimethylselenoacetamide [47].

From these data it appears that the conjugation ability of the thiocarbonyl (and selenocarbonyl) group is much greater than that of the carbonyl group in corresponding mesomeric systems. All things being equal, contribution of the $N=C-\bar{Y}$ valence structure depends on the energy needed in going from (C=Y) to $(C-\bar{Y})$, which can be approximated by $E_{\pi}(C=Y) - A(Y)$ (see ref. 48). It is known that the electron affinity of sulphur is higher (A = 2.077 eV) than that of oxygen (A = 1.462 eV) [49], and the π -bond energy weaker for C=S than for C=O (202.9 and 301.2 kJ mol⁻¹, respectively, [22]). This accounts for the order observed for m_b and m_a , m_b^* and m_a^* , 1.29 > 0.83 and 2.75 > 1.25 respectively. Accordingly, the β (C=S) Hückel resonance integral should be much smaller than β (C=O) [17, 50].

The preferred conformations of tetramethylurea and tetramethylthiourea

For tetramethylurea and tetramethylthiourea, planar models are precluded since the actual $C \cdots C$ distance (2.6 Å) is much shorter than the sum of the van der Waals radii for methyl groups (2 × 2.0 Å [22]). Assuming a C_2 model for these sterically hindered ureas, the dipole moments in benzene (3.50 and 4.65 D [9]) are consistent with mesomeric moments, M, 0.58 or 0.55 D lower than those (1.59 and 3.40 D) of N,N'-dimethylimidazolidin-2-one and N,N'-dimethylimidazolidine-2-thione. A marked decrease in the N—C=Y conjugation energy, with respect to the value in possibly planar ureas and thioureas, is shown by the low barrier to rotation (26.4 kJ mol⁻¹) of the dimethylamino group in both tetramethylurea and tetramethylthiourea [51], compared to the values in N,N-dimethylurea (44.5 kJ mol⁻¹ [44]) and N,N-dimethylthiourea (51.2 kJ mol⁻¹ [46]). Rotational barriers lower than 27.2 kJ mol⁻¹ were suggested by Jensen and Sandström for tetramethylurea, tetramethylthiourea and tetramethylselenourea [47].

Two non-planar models have been retained for tetramethylurea and tetramethylthiourea (Fig. 5): (i) a conrotatory model of C_2 symmetry having its N_{\sim}

two planar Me₂NC groups rotated by the same angle ϕ from the C=Y

reference plane and (ii) an asymmetrical model in which both Me_2NC groups are pyramidal, with $Me \cdot \cdot \cdot Me$ segments situated above (up) and below (down)



Fig. 5. Models (i) and (ii), described in the text, for tetramethylurea and tetramethylthiourea (R = methyl, Y = O or S).

the reference plane. Both these models should possess a reduced mesomeric moment as compared to the value in a planar model (see ref. 9).

The former model should be preferred because of the following. Electron diffraction supports model (i) for gaseous tetramethylurea (CNC = 117.5°) [52]. The sum of the angles at each nitrogen atom in tetramethylthiourea was found to be only 1.5° less than 360° (see ref. 52), from an X-ray diffraction study [53]. Both tetramethylthiourea ligands exhibit the structure (i) in dichlorobis(tetramethylthiourea)copper(II) (with $\phi \sim 20^{\circ}$) and dinitratobis-(tetramethylthiourea)cobalt(II) [54].

Assuming that the mesomeric moment, M, which is proportional to m(N-C=Y), can be expressed as $M^* = M_0 \cdot \cos^2 \phi$ ($M_0 = M$ for $\phi = 0$)*, the actual mesomeric moments in tetramethylurea and tetramethylthiourea ($M^* = 1.01$ and 2.85 D), if compared to those in N,N'-dimethylimidazolidin-2-one and N,N'-dimethylimidazolidine-2-thione ($M_0 = 1.59$ and 3.40 D), are consistent with models (i) for tetramethylurea and tetramethylthiourea characterized by ϕ rotational angles of 37 and 24°, respectively. A smaller angle in the sulphur derivative was expected due to the much greater mesomeric effect in the N-C=S group than in the N-C=O one, which compensates the greater Me···Y attractions when Y = O.

Note added in proof (10/9/81). A recent electron-diffraction study (L. Fernholt, S. Samdal and R. Seip, J. Mol. Struct., 72 (1981) 217), has shown that both tetramethylurea and tetramethylthiourea in the gaseous phase exhibit a shallow configuration about the nitrogen atoms, with nitrogen pyramid heights of 0.272 and 0.113 Å, compared with 0.49 Å for the tetrahedral C_3N pyramid; slight ϕ rotational angles (not explicitly given) are present for both these compounds in the gaseous state.

EXPERIMENTAL

Materials

Cryoscopic benzene R.P. and Normapur dioxan R.P. (from Prolabo, Paris), were twice recrystallized and dried over metallic sodium: at 30.0°C,

^{*}For mesomeric systems such as X—CH=CH₂, where X is a strongly electronegative electron-donating atom (| α |, the coulombic integral, being large), the charge migration of the X lone pair varies as β^2/α^3 [55]. Since β , the C—X resonance integral, is nearly proportional to the π -overlap integral of C—X, the mesomeric moment varies as $\cos^2 \phi$.

 $d_4 = 0.8687$, $\epsilon = 2.2642$ (referred to 2.2741 and 25.0°C), and $d_4 = 1.0226$, $\epsilon = 2.2055$, respectively.

N-Methylimidazolidin-2-one was prepared by oxidation of *N*-methylimidazolidine-2-thione $(2.6 \times 10^{-2} \text{ mol})$, dissolved in water (150 cm³), with potassium permanganate $(5.3 \times 10^{-2} \text{ M}, 1.5 \text{ l})$ added dropwise over 30 min at 60°C. The reaction mixture was set aside for 1 h, then the manganese dioxide filtered off and the solution concentrated to 50 cm³. After cooling, the solution was filtered again to remove some potassium sulphate; hence, the filtrate was extracted with benzene (50 cm³) and from this *N*-methylimidazolidin-2-one was precipitated by adding petroleum ether (b.p. 40– 60° C): m.p. 110°C (lit. 113–114 [8]). Its IR spectrum (solid state) shows ν (CO) at 1665 cm⁻¹ and ν (NH) at 3200 cm⁻¹. Analysis: Calc. for C₃H₇N₂O: C 48.0, H 8.1, N 28.0; found: C 48.3, H 8.3, N 28.5.

N,N'-Dimethylimidazolidin-2-one was obtained by treating N,N'-dimethylethylenediamine (0.12 mol) in benzene (90 cm³) with phosgene (0.12 mol) and anhydrous potassium carbonate (0.18 mol) in benzene (450 cm³). The reaction mixture was maintained for 2 h on an ice-bath, then at room temperature overnight. After filtration to remove the solid, the solution was concentrated to eliminate benzene by distillation at atmospheric pressure. The residue was distilled at reduced pressure and N,N'-dimethylimidazolidin-2-one was fractionated, b.p. 94–95°C at 10 torr (lit. 65–68° C at 2 torr [7], 94–95°C at 11 torr [8]). Its IR spectrum (liquid between KBr discs) shows ν (CO) at 1690 cm⁻¹. Its ¹H NMR spectrum exhibits CH₂ and CH₃ resonance peaks at 3.31 and 2.80 ppm, respectively, using SiMe₄ as internal standard reference.

N-Methylimidazolidin-2-one, N,N'-dimethylimidazolidine-2-thione and their selenonic analogues were prepared nd purified as previously described [1, 56].

Physical measurements

The IR spectra were recorded on a Perkin-Elmer model 325 spectrophotometer. The ¹H NMR spectrum of N,N'-dimethylimidazolidin-2-one was recorded on a Varian FT-80-A spectrometer operating at a nominal frequency of 80 MHz and at a probe temperature of 32°C; the chemical shifts were digitally computed, using SiMe₄ as internal reference.

The electric dipole moments were measured in the specified solvent at 30.0°C by using the well-known Debye refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios [57]

$$\alpha_{0} = \lim_{(w=0)} \left[\frac{(\epsilon - \epsilon_{1})}{w} \right] \text{ and } \beta = \sum (v - v_{1}) / \sum w$$

where w is the weight fraction of the solute, ϵ and v are the dielectric permittivity and specific volume of the solutions, respectively, and subscript one

refers to the pure solvent as used, i.e. made up in the same way as the solutions. The α_0 value was calculated from the linear function, $\alpha = \alpha_0 + \alpha' w$, obtained by least-squares analysis of the $\epsilon(w)$ polynomial (quadratic) function.

N-Methylimidazolidin-2-one, *N*-methylimidazolidine-2-thione and -2selenone are known to be markedly self-associated in carbon tetrachloride $(K_D = 130, 100 \text{ and } 115 \text{ M}^{-1} \text{ at } 25^{\circ}\text{C}$, respectively [4]). For solutes in dioxan, and to a lesser extent in benzene, the dimerization constants should be decreased (see ref. 24, for ϵ -caprolactam) but, as shown by the α' values, they are still high (see Table 1). Consequently, a large number of dilute solutions (at least 15) was examined for these weakly acidic ureas. Specific volumes were accurately measured with a Digital Microdensimeter DMA 02C (Anton Paar, Graz, Austria).

The distortion polarization of the solute, $_{\rm E}P + _{\rm A}P$, was assumed to equal the molecular refraction $(R_{\rm D})$ calculated by additivity from the bond increments of Vogel et al. [58]. The experimental values, from Δn increments measured with a thermostatted VEB Carl Zeiss interferometer (Jena, D.D.R.) and Δv increments, were found to be in accord, within 0.3 cm³, with the additive figures. The accurate molecular refractions of liquid *N*,*N*-dimethylformamide and *N*-methylpyrrolidin-2-one (19.86 [52] and 26.90 cm³ [13]) only differ by 0.10 cm³ from the calculated values. Such a result was rather unexpected because of the strong mesomeric effect existing in these amides, but it can be explained as follows. If *p* is the weight contribution of the zwitterionic valence structure *Z*, then the predicted optical enhancement should be

$$E_{M} = p [R(Z) - R(C)] = p [R(\dot{N}=C-\bar{O}) - R(N-C=O)]$$

= $p \{3.75 + 1.54 + [R(\dot{N}) - R(N)] + [R(\bar{O}) - R(O)] - (1.57 + 3.32)\}$
= $p [5.29 + (\sim 5.3 - 2.74) + (4.06 - 1.64) - 4.89]$

that is 0.5 cm³ only for p = 0.1.* But, taking $R(N) - R(N) + R(\bar{O}) - R(O)$ as $R(N-\bar{O}) - R(N-O) = 1.78 - 2.43 = -0.65$ cm³ [58] leads to $E_M \sim 0$ (for p = 0.1).

The technique used for the measurement of dielectric permittivities is described elsewhere [61, 62].

For each solute, w_{\max} (given to only three decimal places, though it is known to five or six), α_0 , β (in cm³ g⁻¹), $P_{2\infty}$ and R_D (both in cm³ mol⁻¹) and μ (in Debye units) are given in Table 1.

^{*}Bond refractions and atomic refractions for H and N (1.028 and 2.74 cm³) come from ref. 58; $R(\mathring{N})$ is estimated from N⁵⁺ and N³⁺ values [60], and R(O) - R(O) is also found in ref. 60.

TABLE 1

Physical data from dipole moment determinations of N -methyl- and N,N' -dimethylimida-	
zolidin-2-ones, -imidazolidine-2-thiones and -imidazolidine-2-selenones at 30.0°C	

Solute ^a	Solvent	w _{max}	$\alpha_{o} + \alpha' w$	β	$P_{2\infty}$	$R_{\rm D}$	μ(D) ^b
I _a	Dioxan	0.005	18.6 - 200 w	0.150	332.7	26.0	3.91°
IIa	Benzene	0.005	15.5 + 60 w	0.251	365.6	30.9	4.08 ^đ
Ib	Benzene	0.009	21.5 - 470 w	0.338	502.3	34.3	4.82
I _b	Dioxan	0.011	31.6 — 140 w	0.176	635.6	34.3	5.47 ^e
П _ь	Benzene	0.021	22.35	0.350	583.6	39.3	5.20
Ic	Benzene	0.010	18.3 - 480 w	0.520	597.2	36.5	5.28 ^f
Ic	Dioxan	0.005	26.05	0.347	734.2	36.5	5.89
Iľe	Benzene	0.010	19.55	0.606	686.1	41.5	5.66

^aSee Fig. 1 for the meaning of I and II. ^b1 Debye = 3.336 x 10⁻³⁰ C m. ^cLit.: 4.18 D [8]. ^dLiterature values: 4.05 [7] and 2.58 D [8]; the reason for such a discrepancy is obscure, since Cumper and Pickering's examined sample seems to be pure, having the same boiling point as ours. ^eLit.: 4.74 and 5.53 D in benzene and dioxan, respectively, [8]. ^fLiterature values: 5.19 [7] and 5.24 D [8].

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