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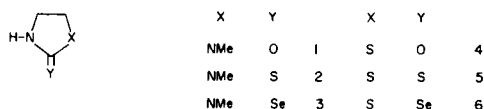
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The hydrogen bonding abilities of *N*-methylimidazolidin-2-one and -2-selone and thiazolidin-2-one and -2-selenone have been studied by ir spectroscopy at 25° in carbon tetrachloride solutions, using dimethyl sulphoxide and 4-chlorophenol as proton acceptor ( $K_A$ ) and proton donor ( $K_B$ ), respectively. The results are compared with those previously reported for *N*-methylimidazolidin-2-thione and thiazolidin-2-thione. The  $K_A$  values increase in each series in the order  $O < S < Se$  and  $K_B$  in the reverse order. The  $K_A$  and  $K_B$  values are discussed in terms of the substituent in ring. The self-association constants ( $K_D$ ) are dependent on both  $K_A$  and  $K_B$ , although  $K_A$  seems to be much more important.

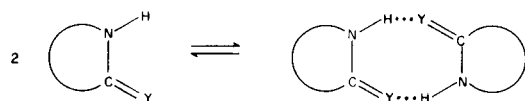
*J. Heterocyclic Chem.*, 16, 1083 (1979).

Recently (1-2), the donor and acceptor ability of the proton of some heterocyclic thioamides have been evaluated by measuring the hetero-association ( $K_A, K_B$ ) and the self-association ( $K_D$ ) constants. In these studies, the influence of the steric and electronic effects of the substituents in the ring on the mentioned constants had been pointed out.

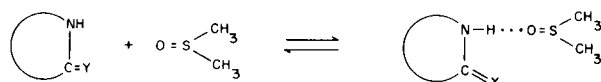
We here wish to report an investigation carried out on thiazolidin-2-one and -2-selenone and on *N*-methylimidazolidin-2-one and -2-selenone, in order to compare the results with those obtained for the sulphur isologues. We shall consider the following molecules:



The association constants have been determined as previously described (1-2);  $K_D$  is the constant related to the formation of a cyclic dimer (1-3):



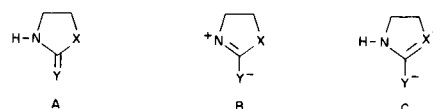
$K_A$  is the equilibrium constant for the reaction with dimethylsulphoxide:



and  $K_B$  is related to the association with 4-chlorophenol:



The results obtained for  $Y = O$  and  $Y = Se$  are reported in the Table, together with those previously obtained for the thioketone ( $Y = S$ ) derivatives (2). As one can see,  $K_A$  increases on passing from oxygen to selenium in both series. The NH proton donor ability  $Se > S > O$  agrees well with a decrease of the positive fractional charge on the NH nitrogen atom (4-6), in accordance with the corresponding decrease of the ionic mesomeric forms B and C on going from selenium to oxygen derivatives.



The different weight to the resonance of the zwitterionic forms for  $Y = O, S, Se$  was hypothesized in the thiazolidine

Table  
Association constants ( $\ell^2 \text{ moles}^{-1}$ ) for  $\text{HN-CH}_2\text{-CH}_2\text{-X-C=Y}$

	X	Y	$K_A$	$K_B$	$K_D$
1	NMe	O	35	600	130
2	NMe	S (a)	42	120	100
3	NMe	Se	75	80	115
4	S	O	110	115	290
5	S	S (a)	200	30	170
6	S	Se	290	45	430

(a) From reference (2).

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series in order to explain the  $\Delta\nu_{\text{NH}}$  values ( $\Delta\nu_{\text{NH}} = \nu_{\text{NH}}$  free -  $\nu_{\text{NH}}$  associated) in their infrared spectra (6). These values (230, 268 and 310  $\text{cm}^{-1}$  for 4, 5 and 6, respectively) have the same trend as those found for  $K_{\Lambda}$ .

On the other hand, the potential barrier to the rotation around the C-N bond increases in the order  $\text{O} < \text{S} < \text{Se}$ . For example, for  $\text{MeC}(\text{Y})\text{NMe}_2$  the  $\Delta G^\ddagger$  values are 19, 21.6 and 22.8 Kcal/mole for  $\text{Y} = \text{O}, \text{S}$  and  $\text{Se}$ , respectively (7-8).

Recently (6,9-12), the influence of the X substituent in ring on the C=Y bond has been discussed for several pentaatomic rings ( $\text{X} = \text{CH}_2, \text{O}, \text{S}, \text{NH}, \text{NMe}$  and  $\text{NEt}$ ;  $\text{Y} = \text{S}, \text{Se}$ ) by infrared spectroscopy. It was pointed out that imidazolidines (9-10) ( $\text{X} = \text{NH}, \text{NMe}, \text{NEt}$ ) behave differently from thiazolidines (6,11) ( $\text{X} = \text{S}$ ), oxazolidines (6) ( $\text{X} = \text{O}$ ) and pyrrolidines (12) ( $\text{X} = \text{CH}_2$ ). In fact, the  $\nu_{\text{CS}}$  and  $\nu_{\text{CSe}}$  stretching vibrations contribute considerably to the bands falling below 600  $\text{cm}^{-1}$  in the imidazolidines, whereas in the other series they give important absorptions also around 1000  $\text{cm}^{-1}$ . This difference was interpreted as due to a low contribution to the resonance of the zwitterionic form C in oxazolidines and thiazolidines, and to the absence of C in the case of the pyrrolidine series. In terms of the low contribution of C to the resonance, it is possible to explain the higher values of  $K_{\Lambda}$  for thiazolidines than for imidazolidines. In fact, the formal positive charge is localized on the two nitrogen atoms in the imidazolidines and on only one in the thiazolidines; consequently one would expect a higher positive charge on this last nitrogen atom, although the negative charge on Y is higher in imidazolidines than in thiazolidines (10-11).

Analogous arguments were produced by Lang (13) to explain the different basicity of the sulphur and nitrogen in thiourea and thioacetamide.

From this, the thiazolidines in contrast with the imidazolidines would exhibit higher  $K_{\Lambda}$  and lower  $K_{\text{B}}$  values, as found. As shown in the Table, the  $K_{\text{B}}$  values vary in the reverse order than  $K_{\Lambda}$ , the selenium compounds being weaker proton acceptors than the oxygen ones. In this case, the  $K_{\text{B}}$  for sulphur and selenium derivatives are of the same order, while they are very low with respect to the oxygen ones. This affinity of the chalcogen atoms towards the proton is turned over in the formation of charge transfer complexes with iodine (13-14), since the selenium compounds give the strongest bonds with iodine. This different behaviour can be explained assuming that the electronic density of Y (higher for  $\text{Y} = \text{O}$  than for  $\text{Y} = \text{S}$  or  $\text{Se}$ ) is responsible for the hydrogen bondings, whereas the bond with iodine is determined by the polarizability of Y. Finally, 1-3 are better proton acceptors than 4-6, in accordance with the higher negative charge on Y in the imidazolidine series.

The self-association constants,  $K_{\text{D}}$ , are practically of the same order on passing from oxygen to selenium

derivatives for each series. This is understandable since they are a measure of the intrinsic reactivity of each donor and acceptor centre. Really, if the  $K_{\text{D}}$  constants for oxygen and selenium derivatives are close, the proton donor and acceptor centres behave in a different manner, as seen above. However, by considering the  $K_{\text{D}}$  values with respect to  $K_{\Lambda}$  and  $K_{\text{B}}$  it is possible to evidenciate that  $K_{\Lambda}$  seems to be more important than  $K_{\text{B}}$  in determining the self-association constants.

To conclude, the knowledge of  $K_{\Lambda}$  and  $K_{\text{B}}$  constants allows to choose the compounds, in bifunctional catalysis, which will be active both for its donor and its acceptor centres. Furthermore, it will be possible to select the couples of compounds which give more stable heterodimers than the corresponding homo-dimers (15).

#### EXPERIMENTAL

N-Methylimidazolidin-2-one (1) and thiazolidin-2-one (4) were prepared according to literature methods (16-17). The selenium compounds were prepared as previously described (6,10).

All spectra were obtained with a Beckman IR9 spectrophotometer at 25°. The spectral slit width was ca. 1  $\text{cm}^{-1}$ . For each compound, three or four solutions were prepared by weighing and diluting. The auto-association and complexation constants were determined as described in the previous papers (1-2).

#### REFERENCES AND NOTES

- (1) E. Gentric, J. Lauransan, C. Roussel and J. Metzger, *J. Chem. Soc., Perkin Trans. II*, 565 (1976).
- (2) E. Gentric, J. Lauransan, C. Roussel and J. Metzger, *ibid.*, 1015 (1977).
- (3) P. F. J. Griffiths, G. D. Morgan and B. Ellis, *Spectrochim. Acta*, 28A, 1899 (1972).
- (4) E. Gentric, unpublished results.
- (5) H. Berthot and A. Pulmann, *C. R. Acad. Sci. Paris*, 262, 76 (1966).
- (6) F. Cristiani, F. A. Devillanova and G. Verani, *J. Chem. Soc., Perkin Trans. II*, 324 (1977).
- (7) H. E. Stewart and T. H. Siddal, *Chem. Rev.*, 70, 517 (1970).
- (8) K. A. Jensen and J. Sandstrom, *Acta Chem. Scand.*, 23, 1911 (1969).
- (9) F. A. Devillanova and G. Verani, *J. Chem. Soc., Perkin Trans. II*, 1529 (1977).
- (10) F. A. Devillanova and G. Verani, *J. Chem. Res. (S)*, 24 (1978).
- (11) F. A. Devillanova, D. N. Sathyanarayana and G. Verani, *J. Heterocyclic Chem.*, 15, 945 (1978).
- (12) F. A. Devillanova and G. Verani, *Aus. J. Chem.*, 31, 2609 (1978).
- (13) R. P. Lang, *J. Am. Chem. Soc.*, 84, 1185 (1962).
- (14) F. A. Devillanova and G. Verani, *Tetrahedron*, in press and references therein.
- (15) E. Gentric, J. Lauransan, C. Roussel and J. Metzger, *Tetrahedron Letters*, 251 (1977).
- (16) A. M. Fusco, G. J. Del Franco and E. J. Aronoff, *J. Org. Chem.*, 31, 313 (1966).
- (17) J. G. Michels and G. Gever, *J. Am. Chem. Soc.*, 78, 5349 (1956).