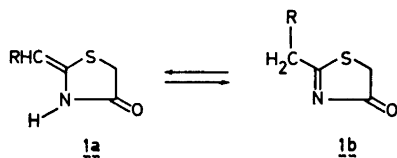


On the Structure of Ethyl 4-Imidazolidone-2-acetate

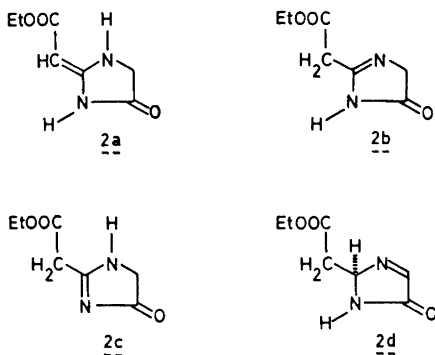
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Investigations on the 2-substituted 4-thiazolidone system have shown¹⁻³ that the $\Delta^{2\alpha}$ -isomer **1a**, having an exocyclic double bond, is the predominating tautomer.* No trace of the Δ^2 -thiazolidinone **1b** could be detected. The isolation of two geometrical isomers of **1a** ($R = \text{COOR}'$) has also been described.²



The present communication describes the synthesis of and similar investigations on the analogous 4-imidazolidone system **2**, for which four tautomeric structures, **2a**, **2b**, **2c**, and **2d** are possible.*



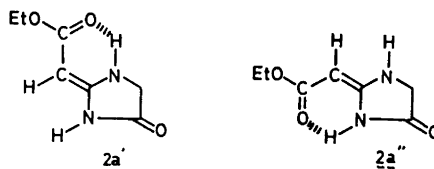
Condensation of ethyl carbethoxyacetimidate⁴ and glycine ethyl ester gave

* Additional tautomeric structures can be written for **1** and **2**, but they do not contain a ring carbonyl group.

the expected substance **2**. The IR spectrum contained two carbonyl bands (1730 and 1695 cm^{-1} ; KBr) and NH absorption (3230 cm^{-1} , broad; 3510 and 3580 cm^{-1} , sharp; dioxane).

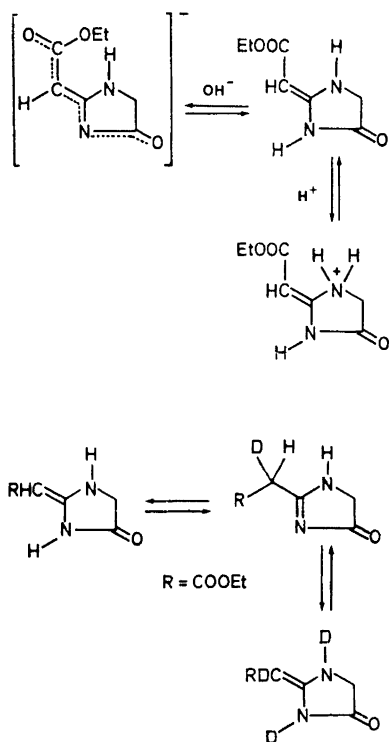
The NMR spectrum of **2** (in dimethyl sulfoxide- d_6) displayed two broad NH bands at 7.80 and 10.90 ppm, as well as unsplit olefinic and CH_2 (ring) absorption at 4.19 and 3.94 ppm, respectively. The last two bands overlap with the CH_2 quartet generated by the ethyl group. These data indicate that **2** exists as **2a** in dimethyl sulfoxide, and that only one geometrical isomer is present.

A solution of **2** in pyridine- d_5 , however, gave rise to two identical, only slightly displaced, sets of signals in the ratio 1:6. Each set contained the same number and types of resonances as did the spectrum of **2** recorded in dimethyl sulfoxide. The chemical shifts (in pyridine- d_5) for the two olefinic proton signals are 4.79 and 4.82 ppm, respectively. These values are too close to be used for assignment of geometrical configurations. It is perhaps reasonable to predict, that the *Z* isomer **2a''**, containing a hydrogen bond involving the more acidic proton, would be the more stable isomer.



The UV spectrum of **2** in ethanol (213 nm; $\epsilon = 11\,900$ and 278 nm; $\epsilon = 30\,000$) is very similar to that of **1a**.² The spectral changes observed for **2** on addition of base (228 nm; $\epsilon = 16\,100$ and 295 nm; $\epsilon = 45\,000$) and acid (282 nm; $\epsilon = 8\,100$) are slightly different from those observed for **1a**.² We therefore propose the following equilibria to explain the acid-base behaviour of **2**.

Participation of the amide proton requires exchange of the olefinic proton in the presence of base. This has earlier been observed in **1a**³ and is also found in **2** along with exchange of the ring-methylene protons when **2** is treated with D_2O and a base such as triethylamine or pyridine.



Our NMR investigations on the 4-imidazolidones were extended also to the 2-methyl and 2-benzyl derivatives **3** and **4**, respectively. While our work was in progress, a detailed report⁵ on the same subject appeared. We have arrived at essentially the same results as Jacquier *et al.*, namely that **3** and **4** have the double bond in the ring and not in the exocyclic position. Apparently, electron-withdrawing groups in the 2-position of the side chain stabilize the double bond in the exocyclic position. In **4**, the resonances for the benzylic and ring-methylene protons appear rather close to one another and Jacquier *et al.*⁵ have assigned them δ -values of 4.05 and 3.77, respectively. Based on lanthanide-shift and spin-decoupling studies, we propose that these assignments should be reversed.

Addition of $\text{Eu}(\text{fod})_3 \cdot d_{27}$ ⁶ to a chloroform-*d* solution of **4** affected the two methylene resonances very differently. The induced shifts for the lower-field

(4.05 ppm) is 14.0 ppm and for the higher-field signal (3.77 ppm) 6.3 ppm. The phenyl protons were divided into two groups with ΔE_{Eu} -values of 2.3 and 1.0 ppm. Good, linear correlation between ΔE_{Eu} and $(3\cos^2\theta_1 - 1)/r_1^3$ (cf. Fig. 1)⁷ is obtained for

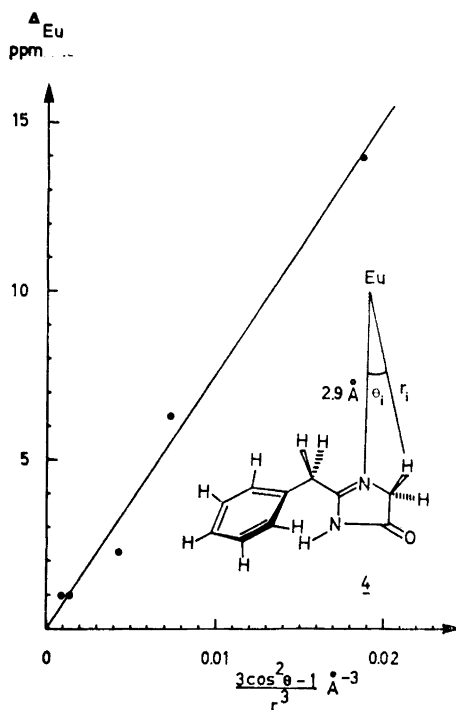


Fig. 1. Plots of the ΔE_{Eu} -values for **4** vs. $(3\cos^2\theta_1 - 1)/r_1^3$ and model showing the localization of the lanthanide ion in **4**.

all protons in **4** if the Eu-atom is placed at a distance of 2.9 Å from N-1 (cf. Fig. 1). The amide-proton signal is too broad to be followed. The diagram published by Wing *et al.*⁸ was used, in combination with Dreiding models, to place the Eu-atom in a position which gave a good, over-all linear correlation. The angles θ_1 and distances r_1 were then refined by error computations. The results indicate that the methylene signal at 3.77 ppm should be assigned to the benzylic protons.

Further support for the above conclusion was rendered by double-resonance studies on **4**. Irradiation of the phenyl protons resulted in distortion of the higher-field

methylene triplet (3.77 ppm), while the lower-field one (4.05 ppm) remained unchanged. Finally, decoupling studies showed that the protons in the two methylene groups indeed coupled with each other.

Synthesis of ethyl 4-imidazolidone- Δ 2 α -acetate.
2. Ten g (0.097 mol) of glycine ethyl ester was slowly (ca. 20 min) added to 15.0 g (0.095 mol) of cold (0°C) carbethoxyacetimidic ethyl ester⁴ in a 100 ml argon-flushed, three-necked, round-bottomed flask, equipped with a gas-inlet tube, a dropping funnel and a drying tube (magnesium sulfate). When the addition was complete, the gas stream was interrupted, the flask stoppered and kept at room temperature in the dark. After 24 h a brown, crystalline solid had precipitated. It was separated by filtration and triturated thoroughly, first with methylene chloride and then with diethyl ether. The brown solid was dried, then recrystallized four times from ethanol. Yield: 3.9 g (24 %) of brownish, flaky crystals. Sublimation of this material (140°C/1 torr) gave white crystals, which turned pink after a short exposure to air and/or light. Freshly sublimed samples were used for all measurements. M.p. 177–180°C, IR (KBr): 3380 (NH), 3300–3100 (NH), 1730 (ring C=O), 1695 (ester C=O), and 1595 cm⁻¹ (C=C), UV (ethanol): λ_{\max} at 278 ($\epsilon=30\,000$) and 213 nm ($\epsilon=11\,900$), NMR (dimethyl sulfoxide- d_6): triplet ($J=7$ Hz) at 1.17 (3H, CH₃), singlet at 3.94 (2H, SCH₂), quartet ($J=7$ Hz) at 4.00 (2H, OCH₂), singlet at 4.19 (1H, =CH), broad peak at 7.80 (1H, NH), and a broad peak at 10.90 ppm (1H, NH). (Found: C 49.03; H 5.81; N 16.12. Calc. for C₈H₁₀N₂O₃: C 49.41; H 5.92; N 16.46). MS: M⁺ = 170.

1. Taylor, P. J. *Spectrochim. Acta* **A 26** (1970) 153.
2. Ceder, O., Stenhede, U., Dahlquist, K.-I., Waisvisz, J. M. and van der Hoeven, M. G. *Acta Chem. Scand.* **27** (1973) 1914.
3. Ceder, O. and Stenhede, U. *Acta Chem. Scand.* **27** (1973) 1923.
4. Lehr, H., Karlan, S. and Goldberg, M. W. *J. Am. Chem. Soc.* **75** (1953) 3640.
5. Jacquier, R., Lacombe, J.-M. and Maury, G. *Bull. Soc. Chim. France* **1971** 1040.
6. Rondeau, R. E. and Sievers, R. E. *J. Am. Chem. Soc.* **93** (1971) 1522.
7. Demarco, P. V., Elzey, T. K., Lewis, R. B. and Wenkert, E. *J. Am. Chem. Soc.* **92** (1970) 5734.
8. Wing, R. M., Early, T. A. and Uebel, J. J. *Tetrahedron Letters* **1972** 4153.

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A New Method for the Preparation of Dianionobis(diamine)cobalt(III) Complexes. Preparation of Carbonatobis(trimethylenediamine)cobalt(III) Salts

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Various methods for the preparation of bis(diamine)cobalt(III) complexes are known. In the following, a new method of preparation for this type of complexes is given. We illustrate the method by giving the preparations of the chloride and nitrate salts of the carbonatobis(trimethylenediamine)cobalt(III) ion.

The traditional method of preparation of the carbonatobis(trimethylenediamine)cobalt(III) ion is based upon the action of carbonate on an aqueous solution of *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride, possibly combined with removal of chloride by treatment with silver carbonate.^{1,2} *trans*-Dichlorobis(trimethylenediamine)cobalt(III) chloride is obtained by air-oxidation of an ethanolic solution of trimethylenediamine (tn) with an excess of anhydrous cobalt(II) chloride in a yield of 43 %.³

The following new method of preparation of carbonatobis(trimethylenediamine)cobalt(III) chloride utilizes hydrated cobalt(II) chloride directly as the starting material and provides a high yield (67 %) of an almost pure sample. An aqueous solution of cobalt(II) chloride (1 mol) is made to react with the carbamate of trimethylenediamine (2 mol) to give a green, not further identified cobalt(II) solution. This cobalt(II) solution is oxidized with hydrogen peroxide. The resulting mixture of bis(trimethylenediamine)cobalt(III) species is by addition of lithium hydroxide combined with a stream of carbon dioxide converted to the red carbonato complex.