# Interaction of 2,4,6-Heptanetrione with 1,5-Diamino-3-Azapentane and Similar Polyamines. The Crystal and Molecular Structure of a New Heterocyclic Compound



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The pathway of the reaction between 2,4,6-heptanetrione and 1,5-diamine-3-aza-pentane was studied and some products identified by ir, uv, mass spectra and x-ray diffractometry. This reaction is not a simple condensation with the formation of a Schiff base but a more complicated process. The structure of the final compound was determined by x-ray crystallography and refined to R = 0.047. Crystals are triclinic, space group $P\bar{1}$, with $a$ = 11.795(5), $b$ = 9.779(5), $c$ = 7.801(5) Å, $\alpha$ = 101.74(3), $\beta$ = 90.93(3), $\gamma$ = 110.65(3), Dx = 1.27 g. cm$^{-3}$ for Z = 2. The structure is essentially formed by three heterorings two of which have a common edge. Only the 4-pyridone ring is planar.

As expected 1,5-diamino-3-thiapentane reacts with the same triketone, in 1:1 or 1:2 molar ratios, to give the acyclic or macrocyclic Schiff bases.

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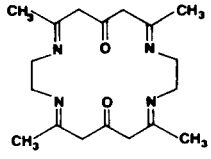
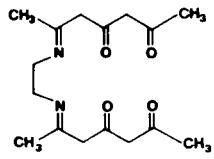
## Introduction.

It is well known that the interaction between 2,4,6-heptanetrione and ethylenediamine gives easily the ring I but not the acyclic compound II [1], which was obtained only by acid hydrolysis of I.

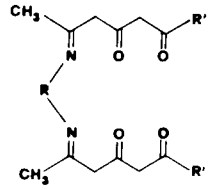


I



II

The acyclic Schiff bases are prepared from asymmetric triketones III, in this case the diamine reacts only with the ketonic group near to $CH_3$ [1-9]:

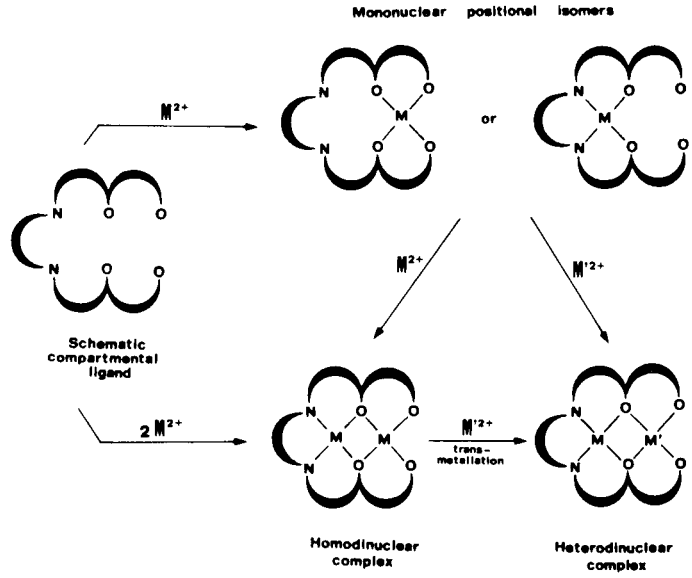


III

R' = phenyl; t-buthyl; etc.
R = aliphatic chain

The open compartmental ketoamines are potentially hexadentate tetraanionic ligands which contain one inner $N_2O_2$, and one outer $O_2O_2$ coordination site.

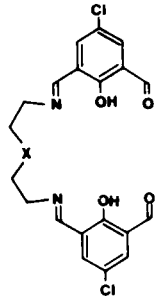
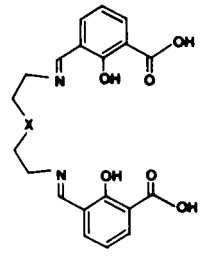
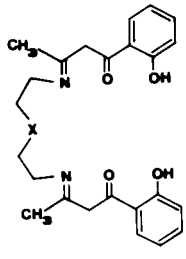
Thus, the metal ions can be coordinated to give mononuclear positional isomers or homo- and heterobinuclear complexes according to the scheme:



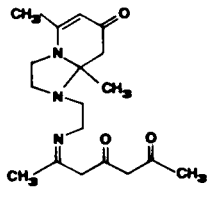

Scheme

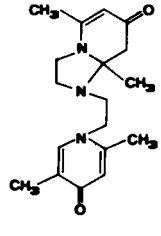
With the aim of enlarging and/or of diversifying the internal sites through the addition of a further donor atom, we have extended the investigation to the reactions of 2,4,6-heptanetrione with polyamines of the type $NH_2$-$(CH_2)_2$-X-$(CH_2)_2$-$NH_2$ (X = NH, S).

Recently we were successful in the preparation of some compartmental ligands [10-13] by reaction of 3-formylsalicylic acid, 4-chloro-2,6-diformylphenol or *o*-acetoacetylphenol with the above polyamines.

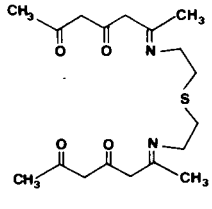




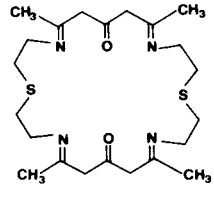
We report here the results of the reaction between 2,4,6-heptanetrione ($H_2$daa) and 1,5-diamino-3-azapentane (dien) which is not a simple condensation with the consequent formation of a Schiff base but a more complicated process. We also compare the resulting products with those obtained by employing the similar polyamines 1,5-diamino-3-thiapentane (sen) or 3,3'-diamino-*N*-methyldipropylamine ($NCH_3$dpp). The compounds identified by reaction of $H_2$daa and dien in a 2:1 molar ratio were **A** and **B**:


A


B

while $H_2$daa with sen gives the open and closed Schiff bases **C** and **D**:


C


D

The structure of **B** was determined by x-ray crystallography.

Table 1

Atomic Coordinates with E.S.D.'s in Parentheses

| Atom | X/A | Y/B | Z/C |
|---|---|---|---|
| N1 | 0.39968(17) | 0.79762(21) | −0.04865(25) |
| N2 | 0.17116(18) | 0.27496(21) | −0.35170(25) |
| N3 | 0.24011(17) | 0.52527(21) | −0.31922(26) |
| O1 | 0.52158(20) | 0.78592(29) | 0.44014(26) |
| O2 | 0.03696(19) | 0.27357(23) | 0.12501(25) |
| C1 | 0.48524(21) | 0.73287(27) | −0.02960(32) |
| C2 | 0.53431(25) | 0.66868(34) | −0.19004(34) |
| C3 | 0.52481(23) | 0.72822(31) | 0.13214(34) |
| C4 | 0.48378(24) | 0.78901(32) | 0.29024(34) |
| C5 | 0.39599(25) | 0.85491(31) | 0.26257(33) |
| C6 | 0.35636(22) | 0.85930(26) | 0.10048(33) |
| C7 | 0.26665(26) | 0.93441(32) | 0.07899(38) |
| C8 | 0.35159(22) | 0.79829(26) | −0.22463(31) |
| C9 | 0.22886(22) | 0.67217(27) | −0.28753(34) |
| C10 | 0.25527(24) | 0.46568(29) | −0.50236(33) |
| C11 | 0.23539(24) | 0.30171(30) | −0.50804(33) |
| C12 | 0.14216(20) | 0.40556(24) | −0.26488(30) |
| C13 | 0.01271(22) | 0.38413(27) | −0.33478(35) |
| C14 | 0.15214(22) | 0.42132(27) | −0.06718(32) |
| C15 | 0.08413(23) | 0.27336(30) | −0.01553(33) |
| C16 | 0.08607(25) | 0.14261(29) | −0.13381(37) |
| C17 | 0.13697(21) | 0.15011(26) | −0.29030(33) |
| C18 | 0.15624(27) | 0.01630(30) | −0.40173(40) |

Calculated Positions for the Hydrogen Atoms

| Atom | X/A | Y/B | Z/C |
|---|---|---|---|
| H92 | 0.16230 | 0.67660 | −0.20380 |
| H131 | −0.00270 | 0.47960 | −0.28440 |
| H91 | 0.19100 | 0.68840 | −0.40540 |
| H81 | 0.35510 | 0.90750 | −0.21370 |
| H82 | 0.40880 | 0.78780 | −0.31360 |
| H51 | 0.36840 | 0.90300 | 0.37050 |
| H132 | 0.00230 | 0.36860 | −0.46970 |
| H31 | 0.59220 | 0.68480 | 0.14270 |
| H73 | 0.19270 | 0.87240 | 0.01520 |
| H112 | 0.31640 | 0.28620 | −0.49770 |
| H141 | 0.24080 | 0.45060 | −0.02520 |
| H133 | −0.04880 | 0.29460 | −0.28790 |
| H183 | 0.11490 | −0.00090 | −0.52840 |
| H182 | 0.11900 | −0.07620 | −0.34830 |
| H161 | 0.05830 | 0.03670 | −0.10470 |
| H181 | 0.24400 | 0.02860 | −0.41900 |
| H101 | 0.19840 | 0.48140 | −0.59560 |
| H71 | 0.24460 | 0.96460 | 0.19620 |
| H142 | 0.11300 | 0.49910 | −0.00070 |
| H21 | 0.59980 | 0.63660 | −0.15700 |
| H23 | 0.57120 | 0.74420 | −0.26490 |
| H111 | 0.17730 | 0.23500 | −0.61690 |
| H22 | 0.47650 | 0.58620 | −0.27650 |
| H102 | 0.33020 | 0.51160 | −0.55680 |
| H72 | 0.31010 | 1.03090 | 0.02110 |

Table 1 (continued)

Thermal Parameters, U(I,J)x10⁴ (e.s.d.'s in parentheses).
Anisotropic Thermal Parameters are in the Form:
$T = \exp[-2\pi^2(U_{ij}h_ih_ja^*_ia^*_j)]$

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N1 | 326(10 | 345(10) | 325(11) | 87( 9) | 58( 9) | 93( 8) |
| N2 | 390(11) | 349(11) | 340(11) | 53( 9) | 80( 9) | 185( 9) |
| N3 | 355(11) | 318(10) | 363(11) | 64( 9) | 51( 9) | 114( 9) |
| O1 | 711(15) | 1216(20) | 359(11) | 264(12) | 97(10) | 485(14) |
| O2 | 651(13) | 662(14) | 435(11) | 179(10) | 222(10) | 206(11) |
| C1 | 305(12) | 417(14) | 380(14) | 101(11) | 76(10) | 109(10) |
| C2 | 467(16) | 693(19) | 372(15) | 54(14) | 79(12) | 297(14) |
| C3 | 381(14) | 579(17) | 401(15) | 134(13) | 60(11) | 211(12) |
| C4 | 425(15) | 618(18) | 354(15) | 137(13) | 75(12) | 155(13) |
| C5 | 466(15) | 565(17) | 334(14) | 44(12) | 98(12) | 197(13) |
| C6 | 338(13) | 349(13) | 421(15) | 47(11) | 76(11) | 101(10) |
| C7 | 503(17) | 535(17) | 552(18) | 30(14) | 69(14) | 268(14) |
| C8 | 410(14) | 339(13) | 344(14) | 120(10) | 39(11) | 103(11) |
| C9 | 372(13) | 340(13) | 470(15) | 81(11) | −27(11) | 123(11) |
| C10 | 511(16) | 456(15) | 335(14) | 117(11) | 129(12) | 163(12) |
| C11 | 503(15) | 482(15) | 335(14) | 65(12) | 94(12) | 239(12) |
| C12 | 320(12) | 282(11) | 342(13) | 46(10) | 47(10) | 132( 9) |
| C13 | 343(13) | 361(13) | 508(16) | 81(12) | −1(11) | 126(10) |
| C14 | 407(14) | 408(14) | 345(14) | 51(11) | 66(11) | 172(11) |
| C15 | 374(13) | 514(16) | 379(15) | 141(12) | 70(11) | 169(12) |
| C16 | 490(15) | 399(15) | 532(17) | 186(13) | 138(13) | 172(12) |
| C18 | 588(18) | 388(15) | 620(19) | 52(13) | 89(14) | 250(13) |

Table 2

Bond Lengths and Angles
A) Bond Lengths (A) (E.S.D.'s in Parentheses)

| | |
|---|---|
| N1 – C1 | 1.388(3) |
| N1 – C8 | 1.479(3) |
| N1 – C6 | 1.389(3) |
| N2 – C11 | 1.467(3) |
| N2 – C12 | 1.473(3) |
| N2 – C17 | 1.334(3) |
| N3 – C9 | 1.461(3) |
| N3 – C10 | 1.468(3) |
| N3 – C12 | 1.466(2) |
| O1 – C4 | 1.254(3) |
| O2 – C15 | 1.238(3) |
| C1 – C2 | 1.502(3) |
| C1 – C3 | 1.353(4) |
| C3 – C4 | 1.426(3) |
| C4 – C5 | 1.433(4) |
| C5 – C6 | 1.354(4) |
| C6 – C7 | 1.510(4) |
| C8 – C9 | 1.526(3) |
| C10 – C11 | 1.528(4) |
| C12 – C13 | 1.541(3) |
| C12 – C14 | 1.517(3) |
| C14 – C15 | 1.526(3) |
| C15 – C16 | 1.424(3) |
| C16 – C17 | 1.373(4) |
| C17 – C18 | 1.508(4) |

B) Bond Angles (Degrees)

| | Angle | E.S.D. |
|---|---|---|
| C6 – N1 – C8 | 119.61 | 0.25 |
| C1 – N1 – C8 | 121.17 | 0.24 |
| C1 – N1 – C6 | 119.19 | 0.24 |
| C12 – N2 – C17 | 120.97 | 0.24 |
| C11 – N2 – C17 | 127.40 | 0.25 |
| C11 – N2 – C12 | 111.60 | 0.23 |
| C10 – N3 – C12 | 106.54 | 0.22 |
| C9 – N3 – C12 | 116.40 | 0.24 |
| C9 – N3 – C10 | 114.49 | 0.23 |
| N1 – C1 – C3 | 120.37 | 0.27 |
| N1 – C1 – C2 | 119.48 | 0.25 |
| C2 – C1 – C3 | 120.15 | 0.28 |
| C1 – C3 – C4 | 123.22 | 0.30 |
| O1 – C4 – C3 | 123.07 | 0.31 |
| C3 – C4 – C5 | 113.94 | 0.25 |
| O1 – C4 – C5 | 122.98 | 0.28 |
| C4 – C5 – C6 | 122.76 | 0.29 |
| N1 – C6 – C5 | 120.51 | 0.29 |
| C5 – C6 – C7 | 120.62 | 0.27 |
| N1 – C6 – C7 | 118.85 | 0.24 |
| N1 – C8 – C9 | 112.45 | 0.23 |
| N3 – C9 – C8 | 111.44 | 0.25 |
| N3 – C10 – C11 | 103.72 | 0.22 |
| N2 – C11 – C10 | 102.71 | 0.23 |
| N2 – C12 – N3 | 99.77 | 0.22 |
| N3 – C12 – C14 | 111.97 | 0.23 |
| N3 – C12 – C13 | 114.91 | 0.23 |
| N2 – C12 – C14 | 109.67 | 0.23 |
| N2 – C12 – C13 | 108.84 | 0.22 |
| C13 – C12 – C14 | 111.02 | 0.24 |
| C12 – C14 – C15 | 112.05 | 0.23 |
| O2 – C15 – C14 | 119.95 | 0.27 |
| C14 – C15 – C16 | 115.35 | 0.26 |
| O2 – C15 – C16 | 124.62 | 0.29 |
| C15 – C16 – C17 | 121.52 | 0.28 |
| N2 – C17 – C16 | 122.00 | 0.27 |
| C16 – C17 – C18 | 121.25 | 0.27 |
| N2 – C17 – C18 | 116.75 | 0.25 |

## EXPERIMENTAL

1,5-Diamino-3-azapentane, 1,5-diamino-3-thiapentane and 3,3'-diamino-*N*-methyldipropylamine were commercial products (Fluka or K & K). They were purified by distillation at reduced pressure and kept in a nitrogen atmosphere. The solvents used were purified according to a literature procedure [14]. 2,4,6-Heptanetrione was synthesized according to the literature [15]. Its purity was checked by elemental analysis, melting point, infrared and $^1$H nmr spectra.

Preparation of **A**.

To an ethanolic solution (40 ml) of 2,4,6-heptanetrione (34.20 mmoles), 1,5-diamino-3-azapentane (17.10 mmoles) in 30 ml of ethanol was added at room temperature. The resulting pale yellow solution was stirred for 2 hours until a yellow precipitate was obtained; this was collected by centrifugation, washed three times with anhydrous ethanol and dried in vacuum, yield = 66%, mp 149-151°.

*Anal.* Calcd. for $C_{18}H_{27}O_3N_3$: C, 64.86; H, 8.11; N, 12.61. Found: C, 64.49; H, 8.39; N, 12.49.

Preparation of *B*.

Crystals of **B**, suitable also for an X-ray investigation, were obtained by slow evaporation (≅ 3 weeks) of a saturated ethanolic solution of **A**.

The crystals obtained were washed with anhydrous diethyl ether, mp 179-182°.

*Anal.* Calcd. for $C_{18}H_{25}N_3O_2$: C, 68.54; H, 7.48; N, 13.32. Found: C, 68.41; H, 8.02; N, 13.51.

Preparation of **C**.

To an ethanolic solution (20 ml) of 2,4,6-heptanetrione (3.6 mmoles), 1,5-diamino-3-thiapentane (1.8 mmoles) in ethanol (20 ml) was added dropwise. The yellow solution obtained was stirred at room temperature for 2 hours. The yellow oil, obtained by partial evaporation of the solvent at reduced pressure, was washed three times with diethyl ether and dried in vacuum.

*Anal.* Calcd. for $C_{18}H_{28}O_4N_2S$: C, 58.69; H, 7.61; N, 7.61; S, 8.70. Found: C, 58.31; H, 7.77; N, 7.55; S, 8.85.

Preparation of **D**.

To a methanolic solution (25 ml) of 2,4,6-heptanetrione (2.78 mmoles) 1,5-diamino-3-thiapentane (2.78 mmoles) in the same solvent (25 ml) was added. The resulting yellow solution was stirred at room temperature for 1 hour until a yellow precipitate was obtained. This was collected by filtration, washed three times with methanol and dried in vacuum, yield 65%, mp 110-111°.

*Anal.* Calcd. for $C_{22}H_{36}N_4O_2S_2$: C, 58.41; H, 7.96; N, 12.39; S, 14.16. Found: C, 58.32; H, 8.05; N, 12.27; S, 13.92.

Physico-Chemical Measurements.

The thermogravimetric and differential thermoanalysis curves were obtained by a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml $min^{-1}$; heating rate 5° $min^{-1}$) and in air flux under the same conditions. Neutral alumina (C. Erba product) was used as reference material. The mass spectra were performed on a VG ZAB-2F instrument.

X-Ray Data.

A well formed single crystal was mounted on a glass fibre with epoxy adhesive and used for the X-ray work. Crystal data are: $C_{18}H_{25}N_3O_2$, FW = 315.4, **a** = 11.797(5), **b** = 9.779(5), **c** = 7.801(5) Å $\alpha$ = 101.74(3)°; $\beta$ = 90.96(3)°, $\gamma$ = 110.65(3)°, **V** = 821 $A^3$, $D_x$ = 1.27 g $cm^{-3}$ for Z = 2, $\mu$(MoK$\alpha$) = 0.5 $cm^{-1}$ triclinic, space group $P\bar{1}$.

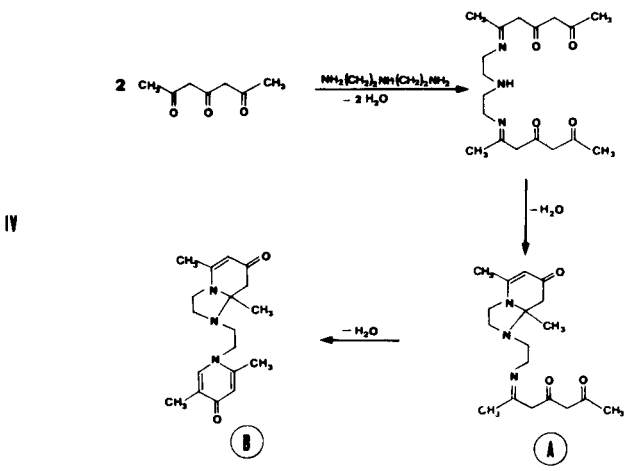
Unit-cell parameters and the intensity data were measured on a Philips-1100 diffractometer using MoK radiation ( = 0.7107 Å). Lattice parameters were refined by least-squares fit to measured 2 values for 25 medium angle reflexions. The intensities were measured up to $\theta$ = 25° using $\omega$-2$\theta$ scans. A total of 3782 reflexions were recorded at a scan speed of 0.03° $sec^{-1}$. No crystal deterioration was observed during irradiation. The measured intensities were corrected for Lp and for absorption [16], and 2252 independent reflexions with I > 3 (I) were used in subsequent calculations. All atoms were located using the automatic centrosymmetric method included in SHELX [17].

Least-squares refinement minimizing $\Sigma w(\Delta F)^2$ with non-hydrogen atoms having anisotropic temperature factors converged to the final agreement index R = 0.047 for the observed data.

Scattering factors for C, N, H and O were supplied internally by SHELX, [17].

## Results and Discussion.

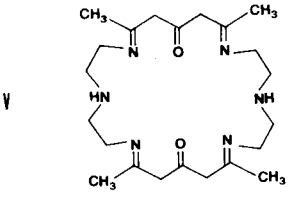
The reaction in ethanolic solution of 2,4,6-heptanetrione with 1,5-diamino-3-azapentane, in the 2:1 or 1:1 molar ratios does not give the usual open and closed ketoamines respectively. The proposed pathway IV for the above reaction in the 2:1 molar ratio is:



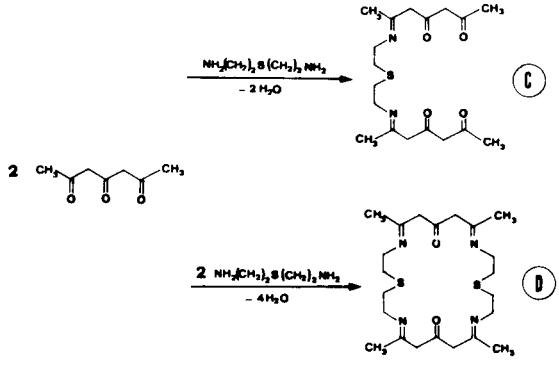
where the first stage of this reaction scheme is supposed to be the formation of the Schiff base, although this product was not identified. Mass spectra carried out at different reaction times and in different solvents, instead of the parent peak of the Schiff base, always gave a peak at 333 m/z due to the product **A** obtained by a fast cyclization of the Schiff base with the elimination of a water molecule.

By recrystallization of **A** from an ethanolic solution, crystals of **B** were obtained.

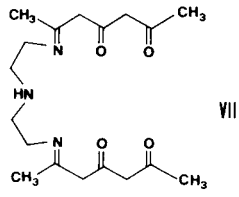
With the 1:1 ($H_2$daa:dien) molar ratio unidentified products were obtained; anyway it was impossible to identify the macrocyclic compound **V**.



When the NH group of the polyamine is substituted by a thioetheric S (*i.e.* employing 1,5-diamino-3-thiapentane) both Schiff bases are obtained according to the Scheme VI:



In addition, by reaction of 3,3'-diamino-*N*-methyldipropyilamine with $H_2$daa in the 1:2 molar ratio, the open Schiff base can be obtained. The parent peak at $P^+ = 393$ m/z due to VII can be detected in the mass spectrum.



VII

These results indicate that in any case the first stage of the reaction between $H_2$daa and a polyamine is the formation of a Schiff base. The subsequent cyclization reaction needs the presence of NH groups; consequently the amines containing sulfur or $NCH_3$ cannot cyclize and form Schiff bases stable enough to give the parent peak also after a long period of time.

For compound **A** we suggest the structure proposed in the Scheme IV, taking into account that the other Schiff bases obtained, which contain the same triketoaminic moiety, do not form a pyridone ring as found for **B**.

Compound **B** probably forms from **A** during the long time required for the formation of crystals. It decomposes during the measurements of mass spectra carried out employing the same experimental conditions as for **A**.

The TG and DTA curves in air and in inert atmosphere of **A** (Figure 1) show an endothermic melting peak at 150°, accompanied by a very small loss of weight (1.58%) immediately followed by an exothermic peak due to decomposition of the sample.

According to the results obtained by thermal analysis, mass spectra of **A** were carried out also at a lower temperature (130°) in order to avoid a possible decomposition or thermal reactions of the sample. The spectra obtained are identical to those obtained at higher temperature (200°).

The infrared spectra of **A** and **B** (Figure 2) show remarkable differences over the range investigated (4000-200 $cm^{-1}$). In particular, the formation of the pyridone ring is reflected by the disappearance in the spectrum of **B** of the band at 3220 $cm^{-1}$ (NH or OH) present in **A**, and by the contemporary appearance of new bands due to $\nu$ C=O at 1621 and 1639 $cm^{-1}$.

Compound **A** is soluble in deuteriochloroform while **B** is not soluble enough for a $^1$H nmr investigation. The $^1$H nmr spectrum of **A** in this solvent shows two N-H peaks at $\delta$ 11.19 and 10.45, three C-H vinylic multiplets at $\delta$ 5.09, 4.95 and 4.70, multiplets due to $CH_2$ centered at $\delta$ 3.63, 3.38, 2.75 and 2.33, and four peaks due to $CH_3$ at $\delta$ 2.04, 2.00, 1.95 and 1.21. The shape of the ir spectra of the acyclic **C** and cyclic **D** compound, obtained by condensation of 2,4,6-heptanetrione and 1,5-diamino-3-thiapentane are very similar; compound **C** has an additional strong band at 1711 $cm^{-1}$, very probably due to the $\nu$ C=O of a not hydrogen bonded carbonyl group.

Both spectra show a very broad band centered at 1580 $cm^{-1}$ for the open **C** and at 1560 $cm^{-1}$ for the closed **D**

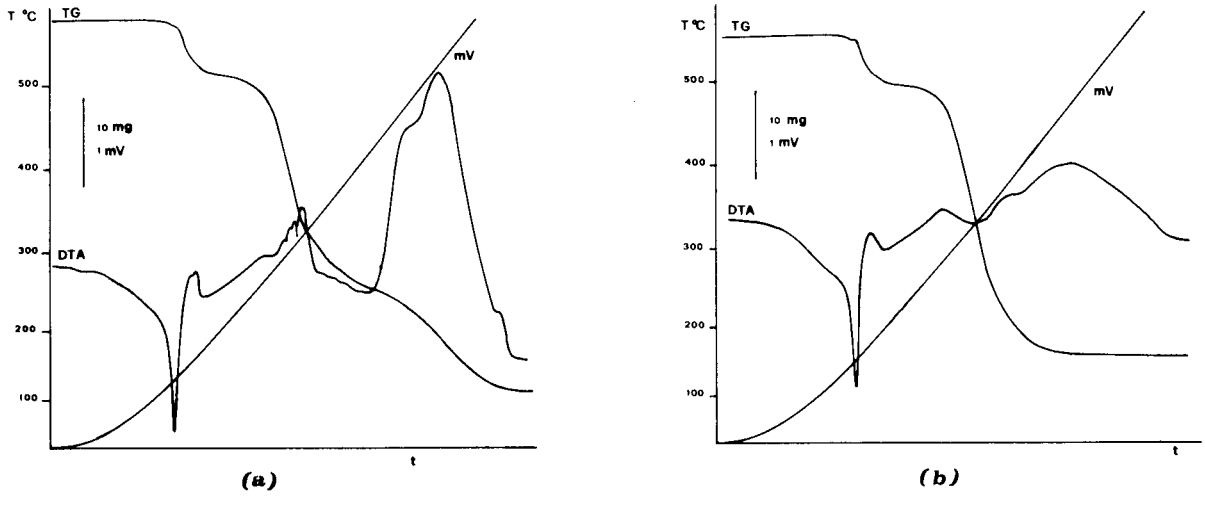



Figure 1. TG and DTA curves of **A**: (**a**) in air, (**b**) in an inert atmosphere.

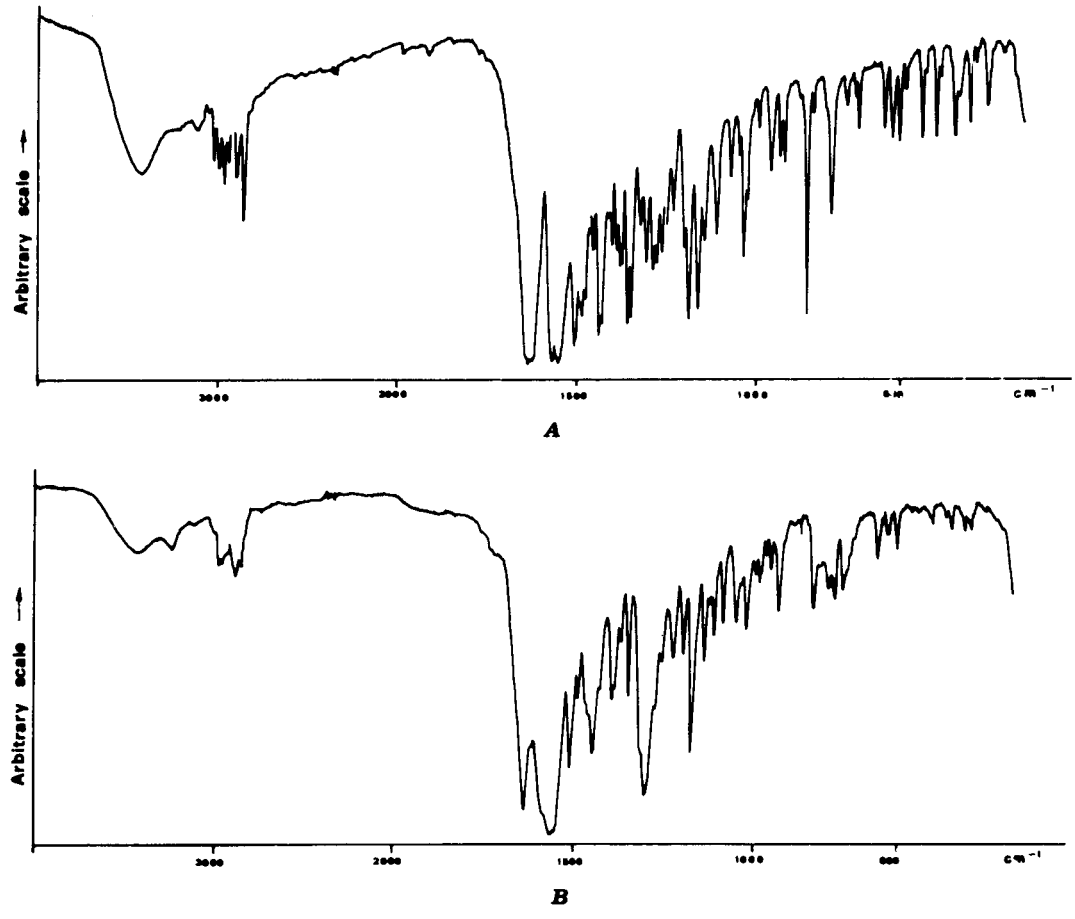



Figure 2. Infrared spectra of **A** and **B**.

compound, due to the absorptions of the contemporary present C=O, C=N and C=C groups.

The nature of **A** was completely understood by the X-ray analysis. As shown in Figure 3 the structure is essentially formed by three etherorings, two of which have a common edge. Four types of C-C bonds are present in the ring skeletons: (a) single $sp^3$-$sp^3$ bonds C(10)-C(11), C(12)-C(14), with a mean length of 1.523 Å; (b) single $sp^3$-$sp^2$ bonds C(1)-C(2), C(6)-C(7), C(14)-C(15), C(17-C(18); the mean of 1.511 Å compares well with 1.505 [18]; (c) single $sp^2$-$sp^2$ bonds C(3)-C(4), C(4)-C(5), C(15)-C(16); the mean value of 1.428 Å is shorter, as expected, than the previous single bonds; (d) $sp^2$-$sp^2$ double bonds C(1)-C(3), C(5)-C(6), C(16)-C(17); the mean value of this bond is 1.360 Å. The conformations of the rings are a direct consequence of the hybridization state of the involved atoms. Thus the 4-pyridone ring, containing only $sp^2$ atoms, is planar, whereas the other two rings have non-planar structures.

The C-N bonds may be divided into three main types. The longest is the single C-N bond; the mean obtained is 1.470 Å. We could not find significant differences between C($sp^3$)-N($sp^3$) and C($sp^3$)-N($sp^2$) bonds in this structure. The second bond type is N to the $sp^2$ C atoms C(1) and C(6), with the possibility of lone-pair electron interaction with the two C=C double bonds of the pyridone ring. The values obtained 1.388 Å and 1.389 Å are fully comparable with the C-N value of 1.383 Å found in pyrrole. The shortest C-N bond N(2)-C(17) of 1.334 Å is also between N and an $sp^2$ C atom, but with the possibility of conjugation of the nitrogen lone-pair with electrons of the C(16)=C(17) double bond.

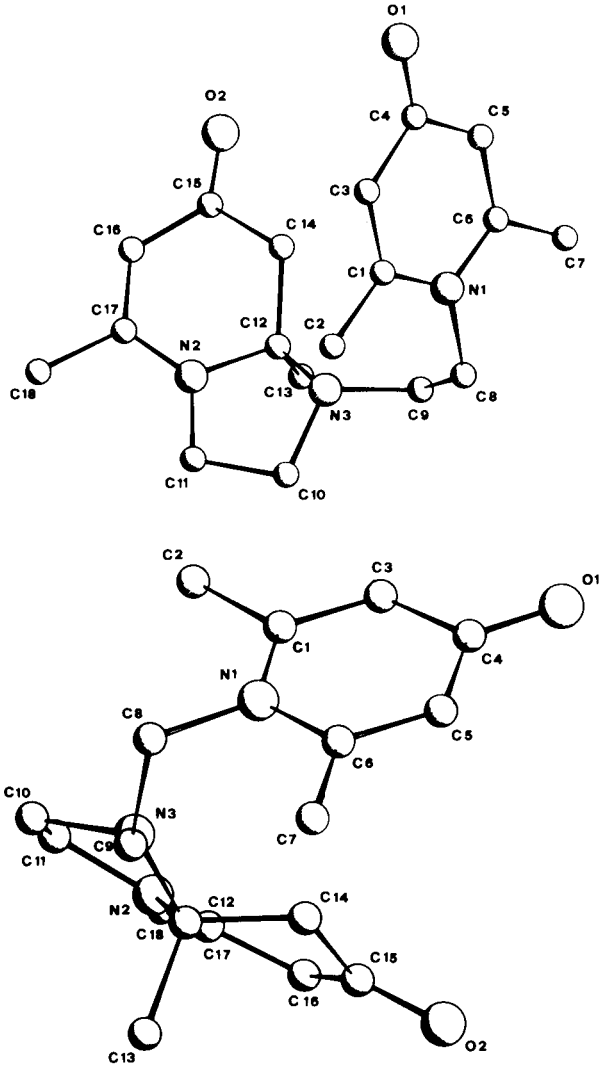



Figure 3. Two perspective views of the molecular structure of **B**.

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