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STEREOCHEMICAL STUDIES—75

SATURATED HETEROCYCLES—62.[1] CONNECTION BETWEEN THE DIASTEREOSELECTIVITY AND THE DOMINANT CONFORMATION IN THE FORMATION OF CONDENSED-SKELETON 1,3-OXAZINES, FIRST X-RAY DIFFRACTION EVIDENCE OF *N-OUTSIDE* CONFORMATION

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Abstract—The rapid, spontaneous epimerization occurring at the C(2) chirality centre of a new diastereomeric (*r*-4,*c*-2,*c*-5)-2-(*p*-nitrophenyl)-3-methyl-4,5-tetramethylenetetrahydro-1,3-oxazine led to the conclusion that the configuration at C(2) of the bicyclic 1,3-oxazines formed by the cyclization of alicyclic 1,3-aminoalcohols with aldehydes is determined by the dominant conformation of the product. The first X-ray diffraction evidence is given for the *N-outside* conformation of compounds of this type.

In earlier papers we have reported the syntheses of a great number of fused-skeleton 1,3-heterocycles by means of the cyclization of alicyclic 1,3-bifunctional compounds (see, e.g. Refs. 2, 3). In the ring closures of *trans*- (1) and *cis*-2-(hydroxymethyl)-1-cyclohexylamine (3) with *p*-nitrobenzaldehyde, a new chirality centre is formed at C(2). The cyclizations were found to occur in a diastereospecific way; aminoalcohols **1a** and **1b** both gave the oxazine **2** containing an *equatorial* aryl group and having the energetically more favoured *r*-4, *c*-2, *t*-5 configuration. Although our work was carried out with racemic compounds, only those enantiomers are shown where the configuration at C(1) in **1** and **3** is R[4]. On the other hand, the *cis*-aminoalcohol **3a** and the *cis*-N-methyl derivative **3b** yielded exclusively the diastereomers with the *r*-4, *c*-2, *c*-5 (**4**) and the *r*-4, *t*-2, *c*-5 (**5**) configuration, respectively.[5,6]

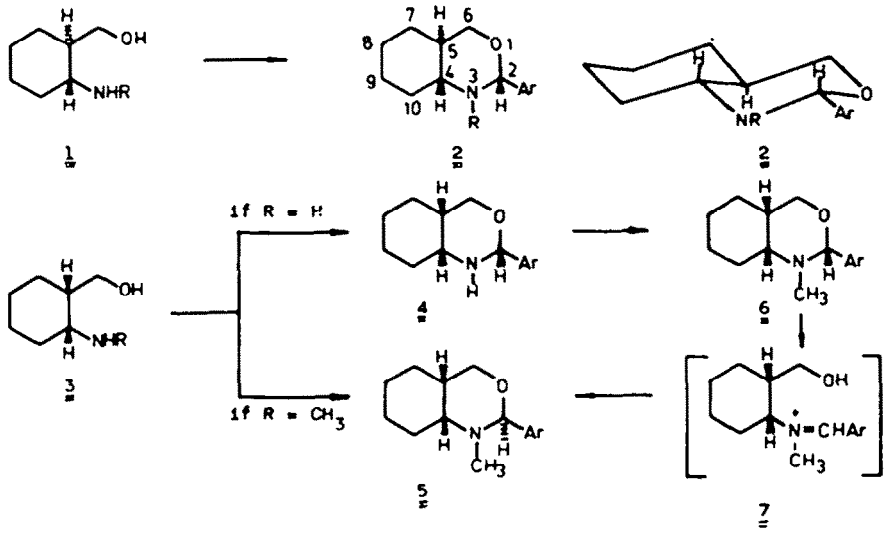
In the present paper the cause of the difference in diastereospecific behaviour in the **3a**→**4** and **3b**→**5** cyclization reactions is described. The ring-closure reactions of **1** and **3** were effected at the b.p. of dioxan, or at room temperature, with acid catalysis. After evaporation of the mixture, the crude products were examined by ^{1}H-NMR spectroscopy and only the oxazine isomers **2**, **4** and **5**, also isolated earlier, were detected.

The synthesis of the new epimeric oxazine **6** was attempted by the N-methylation of **4**, a method described by Boiko *et al.*[7] for analogous oxazines. Treatment in a mixture of formic acid and formaldehyde, however, gave *p*-nitrobenzaldehyde in quantitative yield, instead of the desired **6**, and the liberated aminoalcohol **3a** combined with the formaldehyde to yield *bis*(1,3-oxazine).[8]

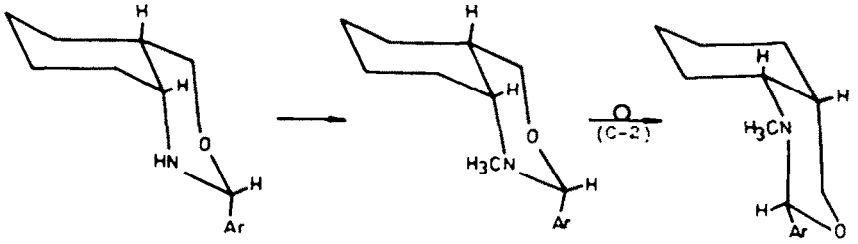
The oxazine **6** was prepared from **4** in acetone, using methyl iodide in the presence of a potassium carbonate. Similar alkylation of the *trans* A/B anellated derivative **2a** gave **2b**. Thus, the identical configuration of **2a** and **2b** was also proved by configurative correlation.

After recrystallization of **6** from hexane, TLC revealed the presence of a new epimeric product, **5**. Examination of the epimerization in $CDCl_3$ solution in an NMR tube showed that at room temperature during one week **6** was converted to **5** (20%). After equilibration for 3 weeks, a mixture (**6**:**5** = 2:1) was attained. In $CHCl_3$ solution, at room temperature, in the presence of one drop of ethanolic hydrogen chloride, epimerization is complete within a few minutes.

NMR spectroscopic evidence was obtained showing the predominance of the N-*inside* conformation of oxazine **4**,[5] and the N-*outside* conformation of **5**.[6] The conformation of the new epimer **6** can be determined by comparison of the ^{1}H NMR spectra of compounds **2**, **5** and **6**. For **6**, a relatively sharp ($\Delta\nu \approx 8$ Hz) signal of H(4) is found at 2.50 δ ppm, whereas the analogous signal in **5** is a doublet of triplets (J = 12.5, 4.8 and 4.8 Hz) at 2.93 δ ppm.



Scheme 1.



Scheme 2.

Consequently, H(4) is *equatorial* in **6** (N-*inside* conformation) (Scheme 2). The anomalous shielding ratio for H(4) (the H(4) *axial* to the cyclohexane ring in **5** is more shielded than the *equatorial* one in **6**) is due to the anisotropy of the hetero-ring: the position of H(4) relative to the hetero-ring is reversed for the epimers. The diamagnetic shift of the H(2) signal ($\Delta\delta$ = 1.13 ppm) is explained by the less crowded structure of **6** as compared with that of **5**. In the crowded compound **5**, H(2) is coplanar with the benzene ring in the dominant rotamer, and the anisotropic effect of the ring in this mutual position reduces shielding around the H(2) atom.

The ^{13}C NMR spectral data (Table 1) for the N-methyl-oxazines **5** and **6** indicate that the higher steric compression in epimer **6** results in a greater shielding of all C atoms than in **5**, with the exception of C(4), C(7) and C(9). The greatest increases in shielding are observed for C(2) and C(6) ($\Delta\delta$ = 11.1 and 5.3 ppm, respectively), as they assume an "in" instead of an "out" position.

We have shown[9] that, of the two possible chair chair conformations, the N-*inside* arrangement is predominant in *cis*-4,5-tetramethylene-3,4,5,6-tetrahydro-1,3-oxazines and -1,3-oxazin-2-ones. Again, for the N-Me derivatives (similarly to the case of **5**[6]) the dominant form is N-*outside* conformation,[10-12] as the *equatorial* arrangement of the bulkier substituent (NCH_3, $NCH_2C_6H_5$) is favoured.[6]

It follows that the new epimer **6** with N-*inside* conformation is energetically unfavoured; therefore on standing it assumes, through the ring-opened[13-15] form **7**, the more stable N-*outside* conformation (Scheme 2). Of course, the change of the dominant conformation involves alteration of the configuration at C(2).

Under the conditions of ring closure, with acid catalysis, the dominant conformation of the products will determine the configuration at C(2) by thermodynamic control, explaining the difference in diastereospecific occurrence in the **3a**→**4** and **3b**→**5** ring-closure reactions.

X-Ray determination of the molecular structure of **5**

Figure 1 shows a perspective view of the structure of **5**, computed from the final atomic coordinates given with their e.s.d.'s in Tables 2 and 3. It shows clearly the relative configurations (*R*, *S*) of the chiral centres C(2) and C(4). Their relative configurations in **4** (possessing also racemic crystal structures[16]) are

Table 1. ^1H and ^{13}C NMR data for compounds **2**, **5** and **6** ($\delta_{TMS} = 0$ ppm) in $CDCl_3$ solution at room temp

^1H NMR (250 MHz)	Comp.	H(2) s(1H)	H(6a) 2xd(1H)[a]	H(6e) 2xd(1H)[a]	H(4)	H(5) m(1H)	H(7,8,9,10) m+s(8H)	H(13,17) m(2H)[b]	H(14,16) m(2H)[b]	NCH_3 s(3H)
	2	5.04	3.40	4.05	2.50[c]	~1.9[d]	0.95(1H) 4.35(4H) 1.55(1H) 1.9(3H)[d]	7.65	8.20	1.95
	5	5.53	3.88	4.06	2.93[e]	~2.6	1.25(2H) 1.55(3H) 1.85(2H) 2.1 (1H)	7.62	8.20	2.15
	6	4.40	3.80[f]		2.50[g]	~2.35	1.2-1.7(6H) 1.8(1H) 2.15(1H)	7.68	8.21	1.88

^{13}C NMR (20.15 MHz)	Comp.	C(2)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	NCH_3	C(12)	C(13,17)	C(14,16)	C(15)
	2	94.9	67.1	35.7	73.5	31.0	26.0	25.5	27.5	30.2	147.3	128.4	123.4	148.1
	5	85.8	61.4	35.9	67.7	27.3	24.8	21.7	28.4	26.1	129.1	127.8	123.3	147.4
	6	96.9	61.2	37.2	72.9	26.2	25.7	19.4	29.5	36.1	131.1	128.9	123.3	148.1

[a] A or B part of ABX spectra (J:11 and 5 Hz)
[b] A or B part of AA'BB' spectra (J:9 Hz)
[c] Half-bandwidth is 25 Hz
[d] Two overlapped multiplets
[e] Double triplet (J: 12.5, 4.8 and 4.8Hz)
[f] Doublet (2H), (J:1.6 Hz)
[g] Half-bandwidth is 8 Hz

Table 2. Atomic coordinates (× 10^4) for non-hydrogen atoms. E.s.d.'s are given in parentheses

	x/a	y/b	z/c	B_{eq} (Å^2)
O(1)	2886(5)	585(7)	5379(2)	5.2(2)
C(2)	2052(6)	-725(9)	4970(3)	3.7(3)
N(3)	2629(5)	-2605(8)	4899(2)	4.4(2)
C(4)	2826(6)	-3630(10)	5546(3)	4.1(3)
C(5)	3662(6)	-2244(10)	5987(3)	5.0(3)
C(6)	3063(7)	-278(10)	6033(3)	5.0(3)
C(7)	3817(8)	-3105(12)	6690(3)	6.2(4)
C(8)	2498(8)	-3847(10)	6940(3)	5.4(3)
C(9)	1828(9)	-5278(12)	6471(4)	6.6(4)
C(10)	1522(7)	-4269(10)	5795(3)	5.2(3)
C(11)	3893(6)	-2541(10)	4525(3)	4.5(3)
C(12)	1798(5)	334(9)	4339(3)	3.6(2)
C(13)	2220(6)	2227(10)	4246(3)	4.3(3)
C(14)	2004(7)	3188(9)	3667(3)	4.5(3)
C(15)	1306(6)	2209(10)	3184(3)	4.1(3)
C(16)	871(6)	330(11)	3256(3)	4.6(3)
C(17)	1087(6)	-614(10)	3838(3)	4.4(3)
N(18)	1055(5)	3267(2)	2571(2)	5.6(3)
O(19)	539(6)	2336(10)	2128(2)	8.5(3)
O(20)	1324(6)	4988(8)	2540(2)	7.4(3)

B_{eq} = 4/3*trace(B*G) where G is the direct metric tensor

Table 3. Atomic coordinates (× 10^3) for hydrogen atoms

	x/a	y/b	z/c	B_i (Å^2)
H(2)	111	-84	518	4.8
H(4)	334	-457	551	5.0
H(5)	473	-250	584	5.8
H(6A)	221	-41	615	6.1
H(6B)	359	43	633	6.1
H(7A)	418	-207	701	7.0
H(7B)	445	-416	668	7.0
H(8A)	223	-250	701	6.3
H(8B)	272	-458	739	6.3
H(9A)	90	-572	667	7.9
H(9B)	277	-582	633	7.9
H(10A)	82	-500	549	6.2
H(10B)	86	-304	584	6.2
H(11A)	418	-375	451	5.3
H(11B)	361	-168	418	5.3
H(11C)	473	-209	467	5.3
H(13)	277	291	449	5.1
H(14)	221	457	365	5.3
H(16)	35	-40	287	5.6
H(17)	84	-209	385	5.3

either *S,S* or *R,R*. This difference is depicted in the Newman projections perpendicular to the C(4)–C(5) bond (Fig. 2). The fused rings adopt an almost perfect chair conformation (Table 5). The N(3)-Me group is bound *axially*, while the 4-nitrophenyl moiety assumes an *equatorial* position. C(13) is eclipsed with O(1). The nitro group is slightly (by *ca* 6°) twisted out of the best plane of the phenyl ring. Although the standard deviations are rather high (1.0°) the 4-nitrophenyl group exhibits similar distortions of the

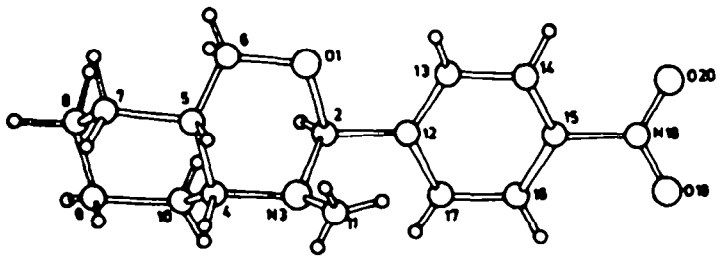
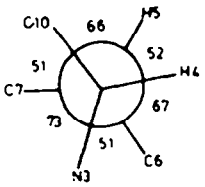


Fig. 1. A perspective view of the molecule 5 with atomic numbering. Bare numbers are for carbonatoms unless indicated otherwise.



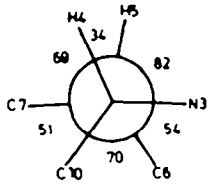


Fig. 2. Newman projections of 4[16] and 5 perpendicular to the *cis* junction.

endocyclic bond angles as found in 4, in accord with the prediction of Domenicano and Murray-Rust.[17]

	Endocyclic bond angle	
	calc.	obs.
at C(12)	118.5	118.7
at C(13) and C(17)	121.3	⟨120.8⟩
at C(14) and C(16)	118.5	⟨118.6⟩
at C(15)	122.1	122.2

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 250 and 20.5 MHz, respectively, in $CDCl_3$ solution with Bruker

Table 4. Bond lengths (Å) and angles (degrees) and their e.s.d.'s in parentheses

O(1)-C(2)	1.475(8)	C(8) -C(9)	1.521(11)
O(1)-C(6)	1.486(7)	C(9) -C(10)	1.585(10)
C(2)-N(3)	1.415(8)	C(12)-C(13)	1.373(9)
C(2)-C(12)	1.511(9)	C(12)-C(17)	1.402(9)
N(3)-C(4)	1.522(8)	C(13)-C(14)	1.381(9)
N(3)-C(11)	1.495(8)	C(14)-C(15)	1.378(9)
C(4)-C(5)	1.545(9)	C(15)-C(16)	1.362(10)
C(4)-C(10)	1.475(9)	C(15)-N(18)	1.478(8)
C(5)-C(6)	1.472(10)	C(16)-C(17)	1.381(9)
C(5)-C(7)	1.577(9)	N(18)-O(19)	1.220(7)
C(7)-C(8)	1.511(11)	N(18)-O(20)	1.206(9)

C(2)-O(1)-C(6)	109.8(8)	C(8) -C(9) -C(10)	111.1(11)
O(1)-C(2)-N(3)	112.6(8)	C(4) -C(10)-C(9)	106.6(10)
O(1)-C(2)-C(12)	106.8(8)	C(2) -C(12)-C(13)	121.7(9)
N(3)-C(2)-C(12)	113.8(9)	C(2) -C(12)-C(17)	119.5(9)
C(2)-N(3)-C(4)	111.6(8)	C(13)-C(12)-C(17)	118.7(10)
C(2)-N(3)-C(11)	112.1(8)	C(12)-C(13)-C(14)	121.8(10)
C(4)-N(3)-C(11)	112.3(8)	C(13)-C(14)-C(15)	117.9(10)
N(3)-C(4)-C(5)	107.3(8)	C(14)-C(15)-C(16)	122.2(10)
N(3)-C(4)-C(10)	110.4(9)	C(14)-C(15)-N(18)	117.4(10)
C(5)-C(4)-C(10)	116.1(9)	C(16)-C(15)-N(18)	120.4(10)
C(4)-C(5)-C(6)	112.5(9)	C(15)-C(16)-C(17)	119.4(10)
C(4)-C(5)-C(7)	111.0(9)	C(12)-C(17)-C(16)	119.9(10)
C(6)-C(5)-C(7)	108.1(9)	C(15)-N(18)-O(19)	116.9(9)
O(1)-C(6)-C(5)	109.9(9)	C(15)-N(18)-O(20)	119.2(9)
C(5)-C(7)-C(8)	112.1(10)	O(19)-N(18)-O(20)	123.8(10)
C(7)-C(8)-C(9)	111.5(11)		

Table 5. Endocyclic and some relevant exocyclic torsion angles (degrees). E.s.d.'s are in parentheses

C(4) -N(3)-C(2) -O(1)	59.9(8)
C(5) -C(4) -N(3) -C(2)	-54.8(8)
C(6) -C(5) -C(4) -N(3)	54.0(9)
C(4) -C(5) -C(6) -O(1)	-56.5(9)
C(5) -C(6) -O(1) -C(2)	57.0(9)
C(6) -O(1) -C(2) -N(3)	-60.0(8)
C(8) -C(7) -C(5) -C(4)	-46.3(10)
C(9) -C(8) -C(7) -C(5)	52.7(10)
C(10)-C(9) -C(8) -C(7)	-60.2(11)
C(8) -C(9) -C(10)-C(4)	60.2(11)
C(9) -C(10)-C(4) -C(5)	-56.6(9)
C(10)-C(4) -C(5) -C(7)	51.2(10)
C(11)-N(3) -C(2) -O(1)	-67.0(8)
C(11)-N(3) -C(4) -C(5)	72.1(9)
C(12)-C(2) -O(1) -C(6)	174.4(10)
C(12)-C(2) -N(3) -C(4)	-178.3(11)
C(13)-C(12)-C(2) -O(1)	-5.0(10)
C(17)-C(12)-C(2) -N(3)	51.6(10)
O(19)-N(18)-C(15)-C(16)	-5.3(10)
O(20)-N(18)-C(15)-C(14)	-8.4(10)

WM-250- and WP 80SY FT-spectrometers at room temp, using TMS as internal standard: sweep width 5 KHz, pulse width 1 and 3.5 μs, acquisition time 1.64 s, relaxation delay 0 and 1 s, computer memory 16 K, number of scans 8 and 1 and 4 K, respectively. Complete proton noise decoupling ($\sim$1 W) for the ^{13}C spectra and Lorentzian exponential multiplication for signal to noise enhancement were used (line width 0.7 and 1.0 Hz). The 2H signal of the solvent was used as lock.

General method for preparing oxazines **2a**, **2b**, **4** *and* **5**. 5 mmol aminoalcohol (**1a**, **b**, **3a**, **b**)[5,12,18] was refluxed with 5.2 mmol *p*-nitrobenzaldehyde in abs dioxan, using one drop of ethanolic HCl as catalyst. After 2 hours the solvent was evaporated. Each crude product was examined by ^1H NMR spectroscopy (see text). The crude residues were recrystallized from n-hexane. Mp's (°C) **2a**: 88–89; **2b**: 102–103; **4**: 126–127; **5**: 122 123 are with good agreement with lit.[5,18] mp's.

If the reactions were performed at room temp, 24 hr was needed for completion of the ring closure.

Oxazine **4** *methylation by Boiko*[7] *method*. 2.4 ml 38% aqueous formaldehyde soln and 0.55 ml 85% formic acid was heated with 0.01 ml (2.62 g) of **4** on a water bath. After 2 hr the mixture was cooled and neutralized with 10% NaOHaq sodium hydroxide. The yellow ppt was identified as *p*-nitrobenzaldehyde.

Starting from **2a**, under similar conditions, *p*-nitrobenzaldehyde was also isolated.

(r-4, c-2, c-5)-2-(p-*Nitrophenyl*)-3-*methyl*-4,5-*tetramethylenetetrahydro*-1,3-*oxazine* (**6**). 5 mmol (1.31 g) **4** was stirred in acetone (50 ml) in the presence of 10 mmol (1.38 g) K_2CO_3 and 8 mmol (0.5 ml) MeI. After 20 hr stirring at room temp, the mixture was filtered and the filtrate was evaporated. The residue was dissolved in ether and after filtration the filtrate was evaporated. The crystalline product **6** was recrystallized from n-hexane, m.p. 74–75°, yield: 1.02 g (74%). (Found: C, 65.26; H, 7.44; N, 10.06. $C_{15}H_{20}N_2O_3$ requires: C, 65.19; H, 7.30; N, 10.14%). MS of **6**, *m/z* (%): 276 (M$^+$, 59), 275 (12), 233 (31), 165 (17), 155 (11), 154 (100), 125 (11), 110 (65), 96 (21), 95 (17), 83 (12), 82 (21), 70 (12), 69 (18), 68 (18), 67 (12), 57 (21), 42 (37), 41 (19).

(Thanks for the data are due to Dr. József Tamás (MTA KKKI, Budapest).)

(r-4,c-2,t-5)-2-(p-*Nitrophenyl*)-3-*methyl*-4,5-*tetramethylenetetrahydro*-1,3-*oxazine* (**2b**). This was prepared from **2a** as described for **6**. The product **2b** (yield 68%, m.p. 101–103°) was identical with the authentic sample, prepared from **1b** as described above.

Crystal structure determination on (r-4,t-2,c-5)-2-(p-*nitrophenyl*)-3-*methyl*-4,5-*tetramethylenetetrahydro*-1,3-*oxazine* (**5**)

Crystal data. $C_{15}H_{20}N_2O_3$. MW = 276.34, monoclinic, a = 9.958 (2), b = 6.822 (1), c = 20.748 (5), Å, β = 91.39 (2)°, U = 1409.1 (8) Å^3, D_c = 1.303 g.cm^{-3}, Z = 4, F(000) = 592, space group $P2_1/n$ (from systematic absences). Intensities of 1856 independent reflexions were collected in the range $2\theta \leqq 50°$ by an ω–2θ scan on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo K_α (λ = 0.71073 Å) radiation. Cell constants were determined by least squares refinement from the setting angles of 25 reflexions. After data reduction, 1445 reflexion with $I-3.0\,\sigma(I) > 0$ were taken as observed. No absorption correction (μ = 0.85 cm^{-1}) was applied. The structure was solved with the MULTAN[19] programme. The E-map computed with the use of the phase set of 180 normalized structure factors having $E \geqq 1.90$ revealed the positions of 15 atoms. The positions of the missing 5 atoms were located in the subsequent Fourier calculation (R = 0.35). Full-matrix least-squares refinement of the positional and isotropic thermal parameters reduced R to 0.15. At this stage, H positions were generated from assumed geometries and checked by a subsequent difference map calculation. Further anisotropic refinement of heavy atom positions gave a final R = 0.097 (R_w = 0.086). No H positions were refined. They were included with individual isotropic temperature factors in the final structure factor calculations. Scattering factors were taken from *International Tables for X-ray Crystallography*.[20] All calculations were performed on a PDP 11/34 minicomputer with the use of the SDP-34 system of Enraf-Nonius with local modifications.

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