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Synthesis, Spectral, and Structural Characteristics of Cyanohydrines Derived from Aliphatic Cyclic Ketones[1]

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Abstract—A series of cyanohydrines derived from cyclic aliphatic ketones was synthesized by acid-catalyzed nucleophilic addition reaction under the action of potassium cyanide. The products were characterized by means of multi-nuclear NMR spectroscopy (^{1}H, ^{13}C, ^{14}N, ^{15}N), mass spectrometry, elemental analysis, UV–Vis spectroscopy, refraction index measurements as well as vibrational spectroscopy. The structure of the cyanohydrine of cyclohexanone was elucidated by means of single crystal X-ray diffraction.

Keywords: cyanohydrines, synthesis, NMR spectroscopy, X-ray structure determination

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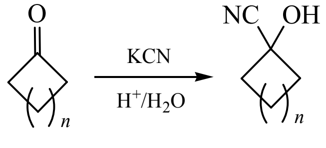
INTRODUCTION

Cyanohydrines, also known as α-hydroxynitriles, are versatile derivatives of aldehydes and ketones. They act as intermediates in the synthesis of a multitude of organic chemicals such as α-hydroxycarboxylic acids [1, 2] and oxazin-2-ones [3]. Historically, cyanohydrines played a major role in solving the stereochemical “cross-word puzzle” posed by the series of carbohydrates in the wake of the Kiliani–Fischer synthesis protocol [4, 5]. The interest in cyanohydrines soared upon their proven applicability in the synthesis of pharmacologically active N-substituted β-aminoalcohols [6]. The latter finding gained particular importance when it was discovered that the enzyme (*R*)-oxynitrilase can be used in converting pro-chiral aldehydes directly and selectively to (*R*)-configured cyanohydrins [7]. The synthesis of cyanohydrines had been traditionally conducted upon the action of pure HCN on the respective carbonyl compounds under acidic conditions [8, 9]. The alternative procedures via the bisulfite adducts of the respective carbonyl compounds were known and deemed to be advantageous for industrial applications [10]. Cyanohydrines have not been extensively studied with regards to their coordination behaviour towards (transition) metals. Among the few examples of cyanohydrine acting as a monodentate anionic ligand which coordination mode had been secured on grounds of single crystal diffraction data are copper [11], manganese [12], and antimony [13] containing compounds. Preliminary accumulation of information on cyanohydrine-supported coordination compounds of transition metals made it evident that despite the long-standing tradition of cyanohydrine synthesis no comprehensive spectroscopic and structural studies focused primarily on this class of molecules had been conducted. This referred also to the simple non-aromatic members of the group. Apart from more complex natural-product-derived cyanohydrines only few structural analyses of simple members of this class of compounds are apparent in the literature [14–16].

The cyanohydrines involved in this study were synthesized upon the acid-catalyzed nucleophilic addition of potassium cyanide to the respective cyclic aliphatic ketones in aqueous medium (Scheme 1).

While the reactions of cyclobutanone, cyclopentanone and cyclohexanone resulted in satisfactory



Scheme 1. Protocol for the synthesis of cyanohydrines **I**–**V** (*n* = 1–5).

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[1] The text was submitted by the authors in English.

to high yields upon application of stoichiometric amounts of reagents, cycloheptanone and particularly cyclooctanone required an excess of potassium cyanide to give high yields of products (Table 1).

All isolated products initially were colourless liquids featuring a faint smell of bitter almonds. Upon storage at room temperature, **III** crystallized spontaneously into a colourless solid with low melting point.

NMR spectra. ^{1}H NMR spectra of compounds **I–V** exhibited complex multiplets for all carbon-bonded hydrogen atoms. The hydrogen atom of the OH group was registered at markedly lower field for **I–IV** (ca 3.75 ppm) than that for compound **V** (3.31 ppm).

^{13}C{^{1}H} NMR data of compounds **I–V** are listed in Table 2. The nitrile group carbon atom signal is not influenced significantly by the size of the ring. The signal of the carbon atom bearing two functional groups was registered at higher field (ca 3 ppm) for the cyclobutanone and the cyclohexanone derived compounds **I** and **III** compared to the compounds **II**, **IV** and **V**. In all compounds a distinctive γ-effect [15] was apparent.

Unlike ^{15}N NMR spectra of **I-V** registered for the neat samples, efforts of accumulation of ^{14}N NMR spectra were unsuccessful. The ^{15}N NMR signals were registered in a narrow range of about 241–244 ppm referred to liquid ammonia.

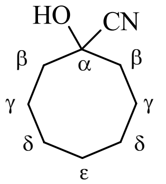

Fig. 1. Labelling of carbon atoms listed in Table 2.

UV–Vis and mass spectra. UV–Vis spectra were recorded for all compounds dissolved in acetonitrile as well as cyclohexane. In all cases $n \rightarrow \pi^*$ excitation was observed, however, the data for the smallest **I** and the largest **V** rings were characterized by the highest energies for this electronic shift (Table 3). The relative effect of the solvent on the observed values was insignificant in all cases but the compound **I** in which the less polar solvent cyclohexane resulted in a more pronounced decrease in energy for the $n \rightarrow \pi^*$ excitation.

Mass spectra of compounds **I–V** recorded in DEI$^+$ mode exhibited in all cases a weak molecular ion peak as well as ions of corresponding fragmentations shedding the hydroxyl and the cyano groups as well as both functional groups. An intensive peak of hydrocyanic acid at 27 mu was recorded in spectra of all compounds that indicated the heat-induced decomposition of the cyanohydrines into the respective

Table 1. Cyanohydrines synthesized and some of their physical characteristics

Comp. no.	Substituent	Yield, %	Boiling point, °C, mbar	Density, g/cm	Refractory index
I	Cyclobutane	75	42 (2.0×10^{-2})	1.02	1.4415
II	Cyclopentane	87	75 (2.0×10^{-2})	1.04	1.4534
III	Cyclohexane	85	90 (2.5×10^{-2})	1.07	1.4616
IV	Cycloheptane	79	94 (2.0×10^{-2})	1.04	1.4568
V	Cyclooctane	70	110 (5.0×10^{-2})	1.04	1.4793

Table 2. ^{13}C{^{1}H} NMR spectra of compounds **I**–**V** in $CDCl_3$. Labelling is indicated in Fig. 1

Comp. no.	CN	C_α	C_β	C_γ	C_δ	C_ε
I	122.0	66.5	36.4	13.0		
II	122.4	73.0	40.6	23.1		
III	122.1	69.6	37.8	22.5	24.5	
IV	122.8	72.3	40.7	21.4	27.6	
V	122.8	72.3	36.1	21.3	24.2	27.5

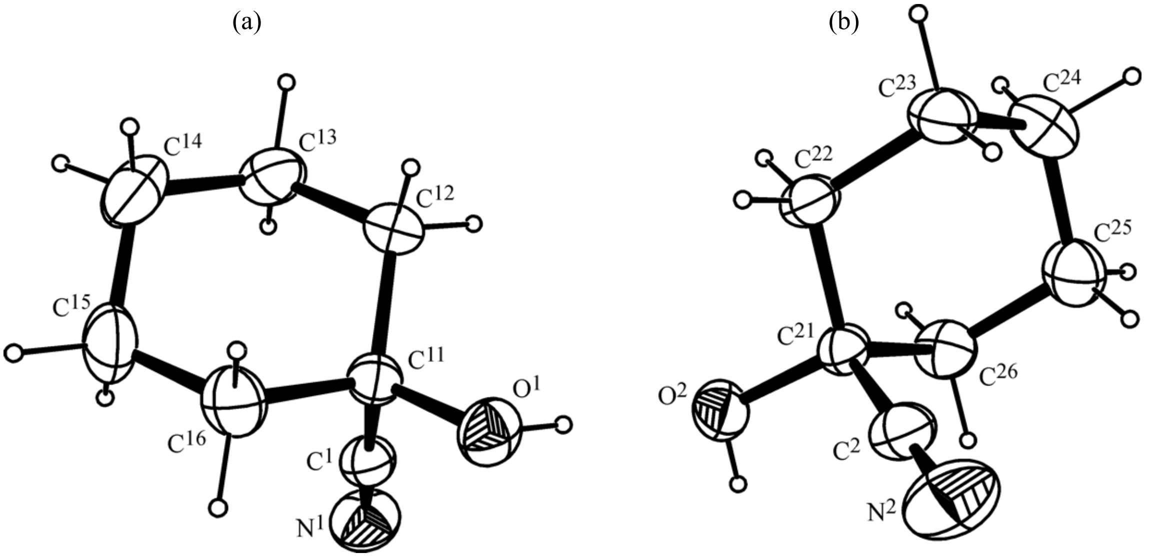

Fig. 2. ORTEP plot of the molecular structure of compound **III** (50% probability ellipsoids). (a) Selected bond lengths (Å) and (b) angles (deg): C^1–N^1 1.1370(13), C^1–C^{11} 1.4964(13), C^{11}–O^1 1.4119(11), C^2–N^2 1.1358(15), C^2–C^{21} 1.4892(14), C^{21}–O^2 1.4246(12); N^1–C^1–C^{11} 178.23(11), N^2–C^2–C^2 1 179.52(13).

ketone to which, formally, the hydrocyanic acid was added nucleophilically in the course of synthesis.

Infrared spectra. Vibrational spectra of all compounds **I**–**V** exhibited one strong and broad band between 3440 and 3410 cm^{-1} for spectra of the "liquid" samples indicating the hydrogen bond of the respective OH groups. An IR spectrum registered for crystalline compound **III** deviated from that profile indicating the presence of two distinct bands at much lower energy (by ca 100 cm^{-1}) due to presence of two different kinds of the hydrogen bond in the solid state. Various ν_{CH} vibrations values, overall, decreased as the size of cyclic substituents increased (Table 4).

X-ray deduced structure of compound III. Compound **III** was the only one to crystallize spontaneously after distillation. Its crystals consisted of two complete molecules in an asymmetric unit (Fig. 2).

Table 3. UV–Vis spectra of compounds **I**–**V** in acetonitrile or cyclohexane

Comp. no.	λ_{max}, nm	
	acetonitrile	Cyclohexane)
I	283	275
II	255	257
III	251	249
IV	222	224
V	288	287

Both cyclohexane rings adopted a $^1C_4$ *chair* conformation [16, 17] ($^{C11}C_{C14}$ and $^{C21}C_{C24}$, respecttively) with the hydroxyl group occupying an equatorial and the cyano group invariably an axial positions. The least-squares planes as defined by the non-hydrogen atoms of the two individual cyclohexyl moieties intersected at an angle of 60.26(4)°. The two C–N bond lengths did not differ significantly [1.1358(15) Å and 1.1370(13) Å]. Such bond lengths were in good agreement with the most common ones reported for this functional group [18]. In the crystals two different types of hydrogen bond (O–H···O and O–H···N) were intermittently connected with two different molecules of the asymmetric unit. Such pattern resulted in formation of centrosymmetric tetramers (Fig. 3).

The C–H···O contact whose range falls by more than 0.1 Å below the sum of van der Waals radii of the atoms participating in it was observed. The latter was apparent between the equatorial hydrogen atom of one of the methylene groups in meta-position to the carbon atom bearing the functional groups as donor of one molecule present in the asymmetric unit and the OH group of its symmetry-generated equivalent as acceptor. Overall, the molecules were connected to undulated sheets parallel [1 0 1]. In terms of graph-set analysis [18, 19], the descriptor for the classical hydrogen bonds was *DD* on the unary and $R^4{}_4$ (14) on the binary level. A description of the C–H···O contacts according to graph-set analysis required a C^1_1 (5) descriptor on the unary level.

EXPERIMENTAL

Reagents and instruments. All reagents were obtained analytically pure from commercial suppliers (Aldrich, Fluka, Sigma, ABCR, etc.) and used without further purification. NMR spectra were recorded on a Bruker Ultrashield 400 Plus spectrometer at 25°C. ^1H and ^{13}C NMR spectra were referenced towards the solvent residual peaks of the deuterated solvents [20]. ^{15}N NMR spectra were referenced towards external liquid NH_3. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer equipped with a Bruker Platinum ATR unit. Mass spectra were measured by a JEOL JMS-700 instrument. Elemental analysis was conducted on an Elementar Vario EL system. UV–Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer. Refractory indices were measured on a Jasco P-1020 Polarimeter. The diffraction studies on single crystals of **III** were performed at 200(2) K on a Bruker Kappa APEX II diffractometer (MoK_α, $\lambda = 0.71073$ Å). Crystals suitable for the diffraction study were picked up directly from the crystallized reaction product. Structure solution and refinement were conducted by means of the SHELX program suite [21] and succeeded in the monoclinic space group $P2_1/c$ [$a = 11.7386(9)$ Å, $b = 11.0146(7)$ Å, $c = 12.3887(9)$ Å, $\beta = 116.031(2)°$, $V = 1439.32(18)$ Å^3, $Z = 8$, $\rho_{calc} = 1.155$ g cm^{-3}, $\mu = 0.078$ mm^{-1}, size = 0.208 × 0.479 × 0.558 mm]. Hydrogen atoms were calculated using the riding-model approximation and were included in the refinement with their U_H values set to $1.2U_{eq}(C)$ and $1.5U_{eq}(O)$, respectively. Final refinement parameters: $R_{int} = 0.0154$, $wR_2 = 0.1057$, $S = 1.045$, 3559 data, 165 parameters. Metrical parameters discussed for the crystal structure of compound **III** were obtained using PLATON [22], graphical presentations were prepared using Mercury [23] and ORTEP-III [24]. Atomic coordinates, bond lengths and angles have been deposited with the Cambridge Structural Database (CCDC: 1021796).

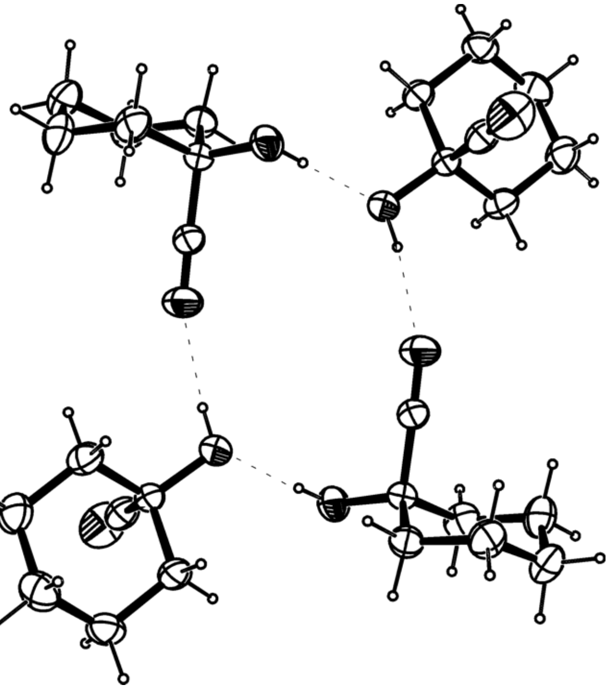

Fig. 3. Centrosymmetric tetramers formed in the crystal structure of compound **III** upon hydrogen bonding (50% probability ORTEP plot) viewed approximately along the crystallographic *c* axis.

Synthesis of compounds I–V *(general procedure).* In a three-necked round-bottomed flask (500 mL) equipped with a dropping funnel and a gas outlet connected with wash bottles filled with sodium hypochlorite solution (first bottle) and ferrous sulfate solution (second bottle), potassium cyanide (200 mmol) was dissolved in water (25 mL) and the cyclic ketone (200 mmol) was added. Upon external cooling with ice and agitation by a magnetic stirrer, a pre-cooled

Table 4. IR bands of selected groups of compounds **I**–**V** (pure liquids)

Comp. no.	ν_{OH}, cm^{-1}	ν_{CH}, cm^{-1}	ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
I	3412	3000–2883	2238	1131
II	3420	2971–2880	2242	1013
III	3439	2942–2864	2240	1039
IV	3427	2932–2861	2238	1043
V	3423	2925–2857	2233	1070

mixture of sulphuric acid (95–98%, 18 mL) in water (32 mL) was added dropwise over the course of 30 min. Formation of an oily layer and a colourless precipitate was observed. Upon completion of the addition, the reaction mixture was stirred for 20 min under persistent cooling. The precipitate was removed by suction filtration and the oily layer was isolated with a separatory funnel. The solid residue was washed twice with diethylether (100 mL each) and the aqueous phase extracted twice with the diethylether used for washing the solid (100 mL each). The combined organic phases were dried over sodium sulphate, filtered and stripped of the solvent in a rotary evaporator. The oily residue was doped with several crystals of chloroacetic acid and distilled under reduced pressure. In each case oily, colourless liquids with a faint smell of hydrocyanic acid were obtained. In case of cycloheptanone and cyclooctanone as the starting materials, the amount of potassium cyanide as well as the sulphuric acid mixture was increased by 50–100% while retaining the original amount of the ketone.

Compound I. Yield 75%, boiling point 42°C (2.0×10^{-2} mbar), ρ 1.02 g/cm^{-3}. ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.68 s (1H, OH), 2.66–2.59 m (2H, CH_2), 2.38–2.29 m (2H, CH_2), 2.02–1.87 m (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.0 (CN), 66.5 (COH), 36.4 (CH_2), 13.0 (CH_2). ^{15}N NMR spectrum (neat), δ, ppm: 241. MS (DEI+) *m*/*z*: 97 ($[M]^+$), 80 ($[M - OH]^+$), 71 ($[M - CN]^+$), 54 ($[M - CN - OH]^+$), 27 ($[HCN]^+$). IR spectrum (neat), ν, cm^{-1}: 3412 s, 3000 m, 2953 m, 2883 w, 2238 w, 1740 w, 1459 w, 1447 w, 1423 w, 1385 w, 1254 s, 1164 s, 1131 s, 1052 w, 1003 w, 963 w, 916 w, 836 w, 793 w. UV–Vis (acetonitrile): 283 nm. UV–Vis (cyclohexane): 275 nm. Refractory index: 1.4415. Found, %: C 61.64, H 7.39, N 14.25. C_5H_7NO. Calculated, %: C 61.84, H 7.27, N 14.42.

Compound II. Yield 87%, boiling point 75°C (2.0×10^{-2} mbar), ρ 1.04 g/cm^{-3}. ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.83 s (1H, OH), 2.10–1.98 m (4H, CH_2), 1.87–1.71 m (4H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.4 (CN), 73.0 (COH), 40.6 (CH_2), 23.1 (CH_2). ^{15}N NMR spectrum (neat), δ, ppm: 241. MS (DEI+) *m*/*z*: 111 ($[M]^+$), 94 ($[M - OH]^+$), 85 ($[M - CN]^+$), 68 ($[M - CN - OH]^+$), 27 ($[HCN]^+$). IR spectrum (neat), ν, cm^{-1}: 3420 m, 2972m, 2880 w, 2242 w, 1637 w, 1452 w, 1439 w, 1393 w, 1322 w, 1208 m, 1094 m, 1065 m, 1013 s, 946 w, 915 w, 883 w, 831 w, 579 w, 489 w. UV–Vis (acetonitrile): 255 nm. UV–Vis (cyclohexane): 257 nm. Refractory index: 1.4534. Found, %: C 64.71, H 7.99, N 12.36. C_6H_9NO. Calculated, %: C 64.84, H 8.16, N 12.60.

Compound III. Yield 85%, boiling point 90°C (2.5×10^{-2} mbar), ρ 1.07 g/cm^{-3} (liquid sample). ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.65 s (1H, OH), 2.08–2.04 m (2H, CH_2), 1.78–1.73 m (2H, CH_2), 1.66–1.47 m (5H, CH_2), 1.30–1.21 m (1H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.1 (CN), 69.6 (COH), 37.8 (CH_2), 24.5 (CH_2), 22.5 (CH_2). ^{15}N NMR spectrum (neat), δ, ppm: 244. MS (DEI+) *m*/*z*: 125 ($[M]^+$), 108 ($[M - OH]^+$), 99 ($[M - CN]^+$), 82 ($[M - CN - OH]^+$), 27 ($[HCN]^+$). IR (neat, solid) ν, cm^{-1}: 3353 m, 3319 m, 2941 m, 2910 w, 2864 m, 2239 w, 1453 m, 1401 w, 1352 w, 1342 w, 1332 w, 1271 w, 1259 w, 1181 w, 1159 w, 1138 w, 1104 w, 1087 m, 1064 s, 1030 m, 971 w, 933 m, 925 m, 904 m, 851 m, 818 w, 788 w, 704 w, 664 m, 608 m, 571 m, 528 m, 459 w, 426 w. UV–Vis (acetonitrile): 251 nm. UV–Vis (cyclohexane): 249 nm. Refractory index: 1.4616 (liquid sample). Melting point (solid sample): 36–38°C. Found, %: C 66.83, H 9.05, N 11.10. $C_7H_{11}NO$. Calculated, %: C 67.17, H 8.86, N 11.19.

Compound IV. Yield 79%, boiling point 94°C (2.0×10^{-2} mbar), ρ 1.04 g/cm^{-3}. ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.91 s (1H, OH), 2.13–2.07 m (2H, CH_2), 1.90–1.84 m (2H, CH_2), 1.71–1.50 m (8H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.8 (CN), 72.3 (COH), 40.7 (CH_2), 27.6 (CH_2), 21.4 (CH_2). ^{15}N NMR spectrum (neat), δ, ppm: 242. MS (DEI+) *m*/*z*: 139 ($[M]^+$), 122 ($[M - OH]^+$), 113 ($[M - CN]^+$), 96 ($[M - CN - OH]^+$), 27 ($[HCN]^+$). IR spectrum (neat), ν, cm^{-1}: 3427 m, 2932 m, 2861 m, 2238 w, 1461 m, 1448 m, 1399 w, 1349 w, 1285 w, 1247 w, 1203 w, 1188 w, 1124 w, 1113 w, 1042 s, 988 w, 957 w, 933 w, 916 w, 888 w, 856 w, 842 w, 799 w, 774 w, 750 w, 586 w, 434 w. UV–Vis (acetonitrile): 222 nm. UV–Vis (cyclohexane): 224 nm. Refractory index: 1.4568. Found, %: C 68.89 (69.03), H 9.15, N 10.14. $C_8H_{13}NO$. Calculated, %: C 69.03, H 9.41, N 10.06.

Compound V. Yield 70%, boiling point 110°C (5.0×10^{-2} mbar), ρ 1.04 g/cm^{-3}. ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.31 s (1H, OH), 2.04–2.02 m (4H, CH_2), 1.72–1.60 m (7H, CH_2), 1.54–1.42 m (3H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 122.8 (CN), 72.3 (COH), 36.1 (CH_2), 27.5 (CH_2), 24.2 (CH_2), 21.3 (CH_2). ^{15}N NMR spectrum (neat), δ, ppm: 242. MS (DEI+) *m*/*z*: 153 ($[M]^+$), 136 ($[M - OH]^+$), 127 ($[M - CN]^+$), 110 ($[M - CN - OH]^+$), 27 ($[HCN]^+$). IR spectrum (neat), ν, cm^{-1}: 3423 m, 2925 s, 2857 m, 2233 w, 1683 m, 1474 m, 1447 m, 1407 w, 1358 w, 1348 w, 1295 w, 1266 w, 1232 w, 1206 w, 1138 w, 1090 w, 1070 m, 1003 w, 933 w, 911 w, 900 w, 871 w, 846 w, 819 w, 808 w, 787 w, 766 w, 744 w. UV–Vis (acetonitrile): 288 nm. UV–Vis (cyclohexane): 287 nm. Refractory index: 1.4793. Found, %: C 70.28, H 9.98, N 8.89. $C_9H_{15}NO$. Calculated, %: C 70.55, H 9.87, N 9.14.

CONCLUSIONS

A series of cyanohydrines derived from aliphatic cyclic ketones has been successfully synthesized and characterized by means of a variety of spectroscopic methods. The accumulated spectral data will support identification of the coordination properties of the aforementioned cyanohydrines in coordination compounds. Multinuclear NMR data will lead to identification of bonding patterns in diamagnetic compounds in solutions. The crystal structure analysis of cyanohydrine derived from cyclohexanone will enable the direct comparison of metrical parameters in the free and the coordinated ligands in envisioned coordination compounds whose metrical parameters will be accumulated on grounds of diffraction experiments with single crystals.

REFERENCES

1. Harnden, M.R., *J. Chem. Soc. C*, 1969, vol. 6, p. 960. DOI: 10.1039/J39690000960.
2. Conley, R.T., *Rec. Trav. Chim. Pays-Bas*, 1962, vol. 81, p. 198. DOI: 10.1002/recl.19620810303.
3. Meerpoel, L. and Hoornaert, G., *Tetrahedron Lett.*, 1989, vol. 30, p. 3183. DOI: 10.1039/J39690000960.
4. Kiliani, H., *Ber. Dtsch. Chem. Ges.*, 1885, vol. 18, p. 3066. DOI: 10.1002/cber.188501802249.
5. Fischer, E., *Ber. Dtsch. Chem. Ges.*, 1889, vol. 22, p. 2204. DOI: 10.1002/cber.18890220291.
6. Noe, C.R., Knollmüller, M., Gärtner, P., Fleischhacker, W., and Katikarides, E., *Monatsh. Chem.*, 1995, vol. 126, p. 557. DOI: 10.1007/BF00807429.
7. Collins, A.N., Sheldrake, G.N., and Crosby, J., *Chirality in Industry*, New York: Wiley, 1992, p. 10.
8. Ultée, A.J., *Ber. Dtsch. Chem. Ges.*, 1906, vol. 39, p. 1856. DOI: 10.1002/cber.190603902124.
9. Urech, F., *Liebigs Ann. Chem.*, 1872, vol. 164, p. 255. DOI: 10.1002/jlac.18721640207.
10. Bucherer, H. and Grolée, A., *Ber. Dtsch. Chem. Ges.*, 1906, vol. 39, p. 1224. DOI: 10.1002/cber.19060390211.
11. Fuller, C.C. and Jacobson, R.A., *Inorg. Chim. Acta*, 1981, vol. 48, p. 191. DOI: 10.1016/S0020-1693(00)90090-2.
12. Sato, Y., Miyasaka, H., Matsumoto, N., and Okawa, H., *Inorg. Chim. Acta*, 1996, vol. 247, p. 57. DOI: 10.1016/0020-1693(95)04942-8.
13. Breneman, G.L., Acta *Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, vol. 35, p. 731. DOI: 10.1107/S0567740879004581.
14. Betz, R. and Klüfers, P., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, vol. 63, p. o3893. DOI: 10.1107/S160053680704127X.
15. Hesse, M., Meier, H., and Zeeh, B., *Spektroskopische Methoden in der organischen Chemie*, New York: Georg Thieme, 1995, p. 146.
16. Cremer, D. and Pople, J. A., *J. Am. Chem. Soc.*, 1975, vol. 97, p. 1354. DOI: 10.1021/ja00839a011.
17. Boeyens, J.C.A., *J. Cryst. Mol. Struct.*, 1978, vol. 8, p. 317. DOI: 10.1007/BF01200485.
18. Etter, M.C., MacDonald, J.C., and Bernstein, J., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1990, vol. 46, p. 256. DOI: 10.1107/S0108768189012929.
19. Bernstein, J., Davis, R.E., Shimoni, L., and Chang, N.-L., *Angew. Chem. Int. Ed. Engl.*, 1995, vol. 34, p. 1555. DOI: 10.1002/anie.199515551.
20. Fulmer, G.R., Miller, A.J.M., Sherden, N.H., Gottlieb, H.E., Nudelman, A., Stoltz, B.M., Bercaw, J.E., and Goldberg, K.I., *Organometallics*, 2010, vol. 29, p. 2176. DOI: 0.1021/om100106e.
21. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112. DOI: 10.1107/S0108767307043930.
22. Spek, A.L., *Acta Crystalogr., Sect. D: Biol. Crystallogr.*, 2009, vol. 65, p. 148. DOI: 10.1107/S090744490804362X.
23. Macrae, C.F., Bruno, I.J., Chisholm, J.A., Edgington, P.R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J., and Wood, P.A., *J. Appl. Crystallogr.*, 2008, vol. 41, p. 466. DOI: 10.1107/S0021889807067908.
24. Farrugia, L.J., *J. Appl. Crystallogr.*, 2012, vol 45, p. 849. DOI: 10.1107/S0021889812029111.