

2-Фениламинотетрагидро-1,3-тиазепин гидрохлориди синтези va спекtral (IQ, YaMR) xususiyatlari

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Annotatsiya. 1-(4-Gidroksibutil)-3-feniltiomochevinaning kislotali muhitdagi halqalanishidan 2-fenilaminotetragidro-1,3-тиазепин гидрохлориди синтез qilindi. Ushbu yangi amino-tautomerga ishqoriy ishlov berish natijasida imin-tautomer - 2-feniliminogeksagidro-1,3-тиазепин olindi. Tautomerlar tuzilishi IQ (FTIR), ¹H va ¹³C YaMR spektroskopiya usullarida tadqiq etildi.

Tayanch so‘zlar: 1-(4-gidroksibutil)-3-feniltiomochevina, 2-fenilaminotetragidro-1,3-тиазепин гидрохлорид, 2-feniliminogeksagidro-1,3-тиазепин, IQ, YaMR spektroskopiya.

Синтез и спектральные (ИК, ЯМР) характеристики гидрохлорида 2-фениламинотетрагидро-1,3-тиазепина

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Аннотация. Осуществлен синтез гидрохлорида 2-фенилтетрагидро-1,3-тиазепина циклизацией 1-(4-гидроксибутил)-3-фенилтиомочевины в

кислой среде. В результате щелочной обработки данного нового аминного таутомера получен иминный таутомер - 2-фениламиногексагидро-1,3-тиазепин. Структуры этих таутомеров изучены методами ИК (FTIR), ^1H и ^{13}C ЯМР спектроскопии.

Ключевые слова: 1-(4-гидроксibuтил)-3-фенилтиомочевина, гидрохлорид 2-фениламинотетрагидро-1,3-тиазепина, 2-фенилиминогексагидро-1,3-тиазепин, ИК-, ЯМР-спектроскопия.

Synthesis and spectral (IR, NMR) characteristics of 2-phenylaminotetrahydro-1,3-thiazepine hydrochloride

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Abstract. 2-Phenylaminotetrahydro-1,3-thiazepine hydrochloride is synthesized by the cyclization of 1-(4-hydroxybutyl)-3-phenylthiourea in acidic media. The imine tautomer, 2-phenylhexahydro-1,3-thiazepine, is obtained when the new amine tautomer is treated with an alkaline solution. The structures of these tautomers are studied using IR (FTIR) and ^1H and ^{13}C NMR spectroscopy.

Keywords: 1-(4-gidroksibutil)-3-feniltiomochevina, 2-fenilaminotetragidro-1,3-tiazepin gidroxlорid, 2-feniliminogeksagidro-1,3-tiazepin, IQ, YaMR spektroskopiya.

Kirish

Organik birikmalar, jumladan, geterotsiklik birikmalar tuzilishi qiziqarli va murakkabligi bilan ajralib turadi. Ayniqsa ularning dinamik izomeriyasi nazariy va amaliy jihatdan muhim bo‘lib, ko‘plab tadqiqotlar ob‘ektiga aylangan.

Tarkibida yetti a'zoli halqa saqlagan 2-fenilaminotetragidro- va 2-feniliminogeksagidro-1,3-tiazepinlar eritmada amin va imin tautomer shakllarda (1-rasm) mavjud bo'lishi mumkinligi sababli ko'plab ilmiy bahslar mavzusi bo'lib qolmoqda [1-3]. Mazkur tadqiqotda 2-feniliminogeksagidro-1,3-tiazepin sintezi amalga oshirilib, uning tuzilishi spektral usullarda isbotlangan.

Mavzuga oid adabiyotlar tahlili. Ba'zi tadqiqotchilar turli xil fizik tadqiqot usullari asosida 1,3-tiazepinlar qatorida amin shaklning mavjudligini isbotlagan bo'lsalar, boshqalari imin shakl haqida dalillar topganlar [1]. Toldi [1] va boshqalar [4-6] tomonidan ushbu tautomer shakllarni o'zaro farqlash uchun $N=C$ guruhining IQ spektrdagi to'lqin uzunligi asosiy omil sifatida qabul qilingan.

Bundan tashqari, 1,3-tiazepin halqalarining maxsus biologik faolliklari qayd etilgan bo'lib, ularning turli hosilalari sintezi amalga oshirilgan [7-13]. Dastlab bir qator 2-ariliminogeksagidro-1,3-tiazepinlar Garmaise va uning hamkasblari tomonidan olingan [14]. Shu bilan birga, 2-benzilaminotetragidro-1,3-tiazepin, 2-feniliminogeksagidro-1,3-tiazepin va uning 3-almashingan hosilalari sintezi haqidagi ma'lumotlar Olszenko-Piontkowa va Urbanski tadqiqotlarida keltiriladi [15]. Ushbu birikmalar N -(1-gidroksibuti1)- N' -benziltiomochevina va N -(1-gidroksibuti1)- N' -feniltiomochevinalarning kons. HCl eritmasidagi halqalanishi natijasida olingan [1]. Ammo, Garmaise [14] bu birikmalarni tiomochevinalarning halqalanishidan olish mumkin emasligini ta'kidlab, ularni 4-brombutil izotiotsiyanatning anilin bilan o'zaro ta'siridan sintez qilgan. Mahsulotlar tuzilishi 1H YaMR spektrdagi $N-CH_2$ bog'i protonlarining signallar asosida imin tautomer shaklda bo'lishi isbotlangan. Keyinchalik, Toldy [1] va Ambartsumovalar [2, 3] tomonidan 1-(4-gidroksibutil)-3-feniltiomochevinaning kislotali muhitdagi halqalanishidan 1,3-tiazepin hosilalarini olish amalda ko'rsatib berilgan. Bir qator gidrogenlangan 1,3-tiazepin hosilalari, jumladan, 2-benziliminogeksagidro-1,3-tiazepin (imin tautomer) Ambartsumova [2, 3] tomonidan sintez qilingan. Ayni birikma (2-

benzilaminotetragidro-1,3-tiazepin) ilgari Olszenko-Piontkowa and Urbanski tomonidan amin tautomer sifatida taklif etilgan edi [15]. Olib borilgan ilmiy munozaralar 1-(4-Gidroksibutil)-3-fenilmochevinaning kislotali muhitda halqalanishi natijasida amin yoki imin tautomer shakl hosil bo'lishi bo'yicha yakuniy xulosalarni ochib bermagan. Shu sababli, 1-(4-gidroksibutil)-3-fenilmochevinaning kislotali muhitda halqalanishi natijasida amin yoki imin tautomer mahsulot hosil bo'lishi batafsil o'rganildi.

Tadqiqot metodologiyasi

Tadqiqotda organik sintez va fizik (spektral) tadqiqot usullaridan foydalanilgan.

Tajribaviy qism

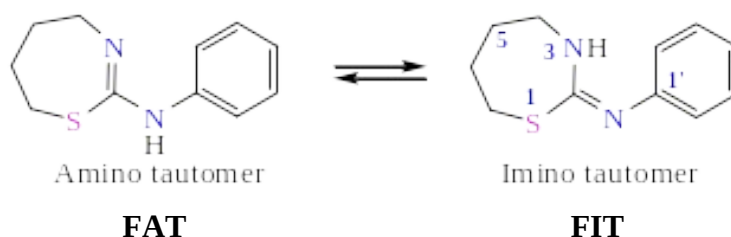
Dastlabki birikmalar – fenil izotiotsianat va 4-amino-1-butanol (Sigma-Aldrich, Merck) qayta tozalanmasdan qo'llanildi. 1-(4-Gidroksibutil)-3-fenilmochevina dastlabki birikmalarning o'zaro ta'siridan adabiyot ma'lumoti asosida sintez qilindi [1, 2] va tuzilishi IQ (FTIR) va ^1H YaMR spektroskopiya usullarida tasdiqlandi [16]. Yog'simon mahsulot reaksiyon aralashmadan ma'lum usulda ajratib olindi [17].

Gidrogenlangan 1,3-tiazepinlar sintezi

1-(4-Gidroksibutil)-3-feniltiomochevina. 1-(4-Gidroksibutil)-3-feniltiomochevina fenil izotiotsianat va 4-amino-1-butanollarning o'zaro ta'siridan ma'lum usulda olindi (1-sxema) [2]. Buning uchun 4-aminobutanol-1 ning (8.91 g, 0.1 mol) TGFdagi (25 mL) eritmasiga fenil izotiotsianatning (13.5 g, 0.1 mol) TGFdagi (15 mL) eritmasi 15-20°C haroratda doimiy aralashtirib turilgan holda tomchilatib qo'shildi. Reaksiyon aralashma xona haroratida 24 soatga qoldirildi. Bunda hosil bo'lgan oq cho'kma filtrlab olindi va etanolning suvli eritmasidan qayta kristallandi. Unum: 90%. Mahsulotning spectral ma'lumotlari adabiyotdagi bilan mos keldi [7].

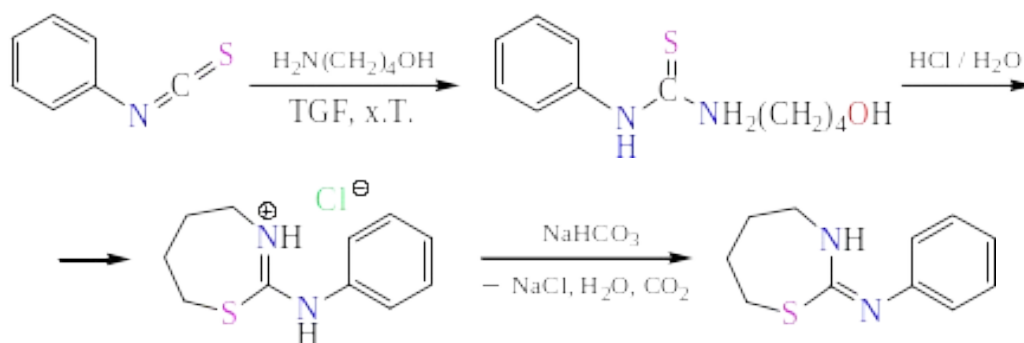
2-Fenilaminotetragidro-1,3-tiazepin gidrokloridi (FATG). Kislotali muhitdagi (kons. HCl) 1-(4-gidroksibutil)-3-feniltiomochevina halqalanishi

adabiyotdagi usul yordamida amalga oshirildi (1-sxema) [1,7,17]. Buning uchun 1-(4-gidroksibutil)-3-feniltiomochevinaga (0.05 mol) kons. HCl (300 mL) qoshib, reaksiya aralashma 5 soat davomida qaynatildi. Xona haroratigacha sovutilgan aralashma hajmi ikki marotaba kamayguncha past bosimda bug'latilib, so'ngra suv (100 mL) qo'shildi, NaHCO₃ (0.1 N) eritmasi ta'sirida (0.1 N) neytrallandi. Hosil qilingan moysimon mahsulot xloroformdan qayta kristallandi, unum 53%.



1-Rasm. Hidrogenlangan 1,3-tiazepinlarning amin va imin tautomerlari: **FAT** - 2-Fenilaminotetragidro-1,3-tiazepin; **FIT** - 2-Feniliminogeksagidro-1,3-tiazepine

2-Feniliminogeksagidro-1,3-tiazepin (FIT). 2-Feniliminogeksagidro-1,3-tiazepin FATGdan quyidagi usulda olindi. FATG (3 g, 0.11 mol) suvda eritilib, NaHCO₃ eritmasi (0.01 N) ta'sirida neytral muhitga keltirildi. Hosil bo'lgan cho'kma filtrlandi, filtrdagi qoldiq xloroformdan qayta kristallandi. Unum 96% (2.27 g).



1-Sxema. 2-Fenilaminotetragidro-1,3-tiazepin gidroxlorigi (FATG) va 2-feniliminogeksagidro-1,3-tiazepin (FIT) sintezi

Sintez qilingan birikmalarning IQ (FTIR) spektri KBr tabletkalarida Nicolet iS10 FT-IR spektrometrida (4000–400 cm⁻¹) to'liq uzunlilari oralig'ida dayd etildi. FTIR spektri Spectragryph-1.2.10 yordamida vizuallashtirildi [18]. ¹H (500 MGs) va ¹³C (125 MGs) YaMR spektrlari CDCl₃ eritmasida (ichki

standart TMS) Bruker 500 MGs YaMR Spektrometrida (Avance Neo) qayd etildi.

Olingan natijalar tahlili.

Gidroxlorid holdagi amin tautomer tuzilishi. Sistematik nomlari (Z)-N-fenil-4,5,6,7-tetragidro-1,3-tiazepin-2-amin va (E)-N-(1,3-tiazepan-2-iliden)-benzenamin birikmalari dastlabki tadqiqotlarda mos ravishda 2-fenilaminotetragidro-1,3-tiazepin (FAT) va 2-feniliminogeksagidro-1,3-tiazepin (FIT) deb nomlangan (1-rasm). Ilmiy bahslar sababli mazkur tadqiqot ishida ushbu birikmalarning trivial nomlaridan foydalanildi. 2-Feniltetragidro-1,3-tiazepin (FATG) gidroxlorid holida ilk marotaba sintez qilindi [19].

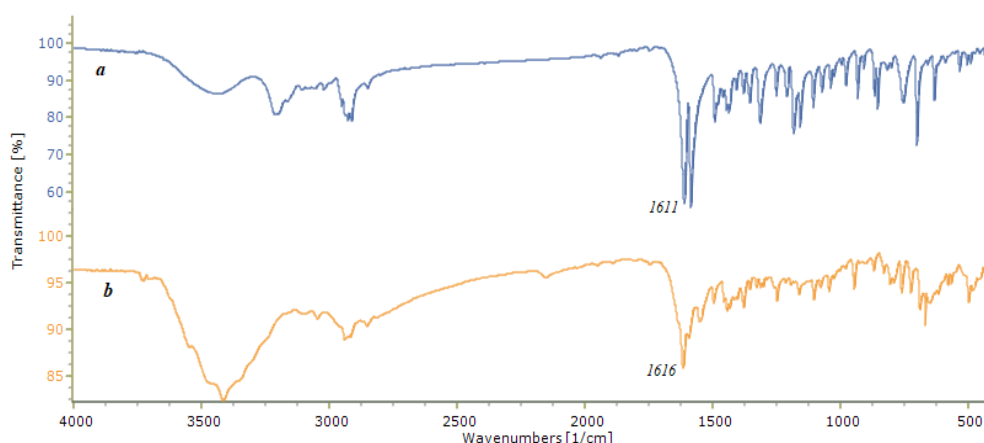
Ma'lumki, amidin guruhi ($N=C-N$) saqlagan birikmalarning tautomer shakllari ekzotsiklik va endotsiklik C-N bog'larning uzunliklarini solishtirish asosida o'zaro farqlanadi [4, 20]. Amidin ($N\equiv C\equiv N$) guruhining azot atomlari o'rtasida kuchli konjugirlanish mavjudligi ulardagi bog' uzunligining o'zgarishiga olib keladi. Bunda $N\equiv C$ bog'ining uzunligi alohida olingan N-C bog'idan qisqaroq. Shuningdek, $N\equiv C$ bog' uzunligi alohida holdagi qo'sh $N=C$ bog'larga nisbatan uzunroqdir [4].

Adabiyotda 1,3-tiazepinning tautomer shakllarini spektral usullar bilan aniqlashda ayrim noaniqliklar ham kuzatiladi. 1,3-Tiazepin misolida [17] keltirilgan usulda reaksiya aralashmadan faqat yog'simon mahsulot ajratib olingan [17].

Mahsulotning katta qismi kristall shaklda olindi. Olingan monokristallar ishqor eritmasi (0.1 N NaOH) bilan ishlanib, neytral FAT olindi. Ammo bu uning spektral ma'lumotlari adabiyotlardagi [3, 21] FIT ning shakllanganligini ko'rsatdi. Bu shuni ko'rsatdiki, imin shakli (FIT) 1,3-tiazepinning neytral (pH=7) muhitdagi dominant tautomer shakli hisoblanadi.

FATGning IQ (FTIR), 1H va ^{13}C YaMR spektrlari qayd etildi va har bir birikmaning xarakterli signallarini aniqlash uchun FIT spektrlari bilan solishtirildi.

Birikmalarning spektrlar xususiyatlari. Shuni ta'kidlash lozimki, FATGning FTIR spektrida $2500-2700\text{ cm}^{-1}$ sohada protonlangan piridin tipidagi azot atomiga mos keladigan yutilish zonasi mavjud emas [22]. FATG va FITlarning C=N guruhlariga mos ravishda 1616 va 1611 cm^{-1} sohalarda kuzatiladi (2-rasm). FIT shaklidagi NH guruhining yutilish chiziqlari $3100-3250\text{ cm}^{-1}$ sohada kuzatiladi, ammo buday yutilish chiziqlari FATGning IQ spektrida aniqlanmadi.



2-Rasm. FIT (a) va FATG (b) larning IQ (FTIR) spektri

Qo'sh C=N bog' to'lqin raqami va C2, C1' uglerod signallarining holati va ularning ^{13}C YaMR spektridagi farqi tautomer shakllarini o'zaro farqlash uchun ishonchli usul sifatida taklif etilgan [17]. 1,3-Tiazinning amin shaklidagi C2 uglerodining signali imin shaklidagi C2 signaliga (152.1 ppm) nisbatan birmuncha kuchsiz maydonda (165.3 ppm) kuzatiladi. Shuningdek, amin shaklidagi C2 va C1' uglerod signallari orasidagi farq ($\Delta\delta=30.6$ m.u.) imin shakliga ($\Delta\delta=5.4$ m.u.) nisbatan juda yuqori. Bunday signaller FATG holatida kuzatilgan. YaMR spektrdagi ^1H va ^{13}C yadrolarining TMS ga nisbatan kimyoviy siljish qiymatlari (1-jadval) shuni ko'rsatadiki, ikkala yadroning signallari amin shakliga nisbatan gidrokslorid holatida ko'proq kuchsiz magnit maydoni sohasida joylashadi. FATGning C2 va C1' uglerod atomlari signallari mos ravishda 173.62 va 135.86 m.u. sohasida kuzatildi. Shu bilan birga, FIT ning ushbu atomlarining signallari 160.12 va 148.93 m.u.da kuzatildi. C2 va C1'

uglerod signallari orasidagi farq FATG va FIT uchun mos ravishda $\Delta\delta=37.76$ va 11.19 m.u.ga teng bo'ldi.

1-Jadval. FIT va FATGlarning tarkibidagi ^1H va ^{13}C yadrolarining YaMR spektridagi kimyoviy siljish qiymatlari (δ , m.u.)

Birikma	^1H YaMR, (CDCl_3 , 500 MGs)							
	NH	H(C4)	H(C5)	H(C6)	H(C7)	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H
FATG	11.98, 10.91	3.69	2.07	1.83	3.00	7.24	7.40	7.34
FIT	6.38*	3.37	1.66	1.96	2.81	6.89	7.25	7.01
^{13}C YaMR (CDCl_3 , 125 MGs)								
Birikma	C2/C1'	C4	C5	C6	C7	C2'	C3'	C4'
FATG	173.62/135.86	46.34	28.57	26.62	33.47	128.34	129.29	125.99
FIT	160.12/148.93	45.31	30.00	30.47	32.17	121.97	128.70	122.81

*Keng signal

Xulosa

Amino-imin tautomerlar sohasida ilmiy munozaralarga sabab bo'layotgan 1-(4-gidroksibutil)-3-fenilmochevinaning kislotali muhitdagi halqalanishidan dastlab 2-fenilaminotetragidro-1,3-tiazepin gidrokslorid hosil bo'lishi, so'ngra ushbu amin tautomerni NaHCO_3 eritmasi ta'sirida neytrallanganda imin tautomer hosil bo'lishi ko'rsatib berildi. 2-Fenilaminotetragidro-1,3-tiazepin gidrokslorid ilk marotaba sintez qilindi. Birikmalarning tuzilishi IQ (FTIR), ^1H va ^{13}C YaMR spektroskopiya usullarida tasdiqlandi. Ushbu tadqiqot natijalari amin-imin tautomerlar bo'yicha ilmiy bahslar yechimida amaliy ahamiyat kasb etadi.

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