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FTORLANGAN β-DIKETONLAR VA 1,3-DIAMINOPROPAN ASOSIDA SHIFF ASOSLARI SINTEZI VA KVANT KIMYOVIY TAHLILI

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Annotatsiya. Ushbu maqolada triftoratsetilatseton (TFAA) va geksaftoratsetilatseton (GFAA) kabi ftorlangan β-diketonlar bilan 1,3-diaminopropan (propilendiamin) asosida sintez qilingan bis-Shiff asoslari (bis-iminlar)ning sintezi va ularning kvant kimyoviy (DFT) parametrlari asosidagi tahlili yoritiladi. Ushbu moddalarning molekulyar orbitallari, elektron zichligi, HOMO-LUMO oralig'i, dipol moment va elektrofilik ko'rsatkichlari hisoblab chiqildi. Asosiy e'tibor ularning elektron tuzilishi, energetik va termodinamik xususiyatlari, reaksion faolligi, shuningdek, donor-akseptor o'zaro ta'sirlari natijasida shakllangan holatlarini aniqlashga qaratilgan. Triftoratsetilatseton (TFAA) bilan hosil qilingan modda UB-VIS spektrda tekshirildi va Geksaftoratsetilatseton (GFAA) bilan olingan moddaning spektr ^{1}H-YMR olindi Mazkur parametrlar asosida olingan natijalar tahlil qilinadi va izohlanadi. Olingan natijalar ularning keyingi kompleks birikmalar uchun yuqori reaktiv ligandlar sifatida salohiyatini namoyish etadi.

Kalit so`zlar: triftoratsetilatseton(TFAH),geksaftoratsetilatseton (HFAH), β-diketonlar ,1,3-diaminopropan (propilendiamin), kvant-kimyoviy hisoblash, DFT, YuBMO, QBMO, dipol momenti, UB-VIS, ^{1}H-YMR.

Аннотация. В настоящем исследовании представлен синтез бис-Шифф оснований (бис-иминов), полученных из фторсодержащих β-дикетонов, а именно трифтороацетилацетона (TFAA) и гексафтороацетилацетона (GFAA), с использованием 1,3-диаминопропана (пропилендиамина) в качестве прекурсора. Молекулярные орбитали, распределение электронной плотности, энергетические разрывы HOMO–LUMO, дипольные моменты и показатели электрофильности синтезированных соединений были систематически рассчитаны с использованием теории функционала плотности (DFT). Основное внимание уделялось изучению электронной структуры, энергетических и термодинамических свойств, реакционной активности, а также конформационных особенностей, формирующихся в

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результате донорно-акцепторных взаимодействий. Соединение, синтезированное из TFAA, было охарактеризовано с помощью UV–Vis спектроскопии, а соединение из GFAA исследовано методом ^{1}H ЯМР. Полученные вычислительные и экспериментальные данные были тщательно проанализированы и интерпретированы, что продемонстрировало потенциал этих соединений как высокореактивных лигандов для формирования координационных комплексов в будущих исследованиях.

Ключевые слова: трифторацетилацетон (TFAH), гексафторацетилацетон (HFAH), β-дикетоны, 1,3-диаминопропан (пропилендиамин), квантово-химические расчёты, DFT, ВЗМО, НЗМО, дипольный момент, UV-VIS, ^{1}H-YMR

Abstract. This study reports the synthesis of bis-Schiff bases (bis-imines) derived from fluorinated β-diketones, specifically trifluoroacetylacetone (TFAA) and hexafluoroacetylacetone (GFAA), using 1,3-diaminopropane (propylene diamine) as a precursor. The molecular orbitals, electron density distributions, HOMO–LUMO energy gaps, dipole moments, and electrophilicity indices of the synthesized compounds were systematically calculated using Density Functional Theory (DFT). Particular emphasis was placed on elucidating their electronic structures, energetic and thermodynamic properties, reactivity, and conformational features arising from donor–acceptor interactions. The TFAA-derived compound was characterized using UV–Vis spectroscopy, while the GFAA-derived compound was analyzed by ^{1}H NMR spectroscopy. The computational and experimental results were critically analyzed and interpreted, revealing the potential of these compounds as highly reactive ligands suitable for the formation of coordination complexes in future studies.

Key words: trifluoroacetylacetone (TFAH), hexafluoroacetylacetone (HFAH), β-diketones, 1,3-diaminopropane (propylenediamine), quantum chemical calculations, DFT, HOMO, LUMO, dipole moment, UV-VIS, ^{1}H-YMR

Kirish

Ftorlangan β-diketonlar organik sintez va koordinatsion kimyoda yuqori reaktivligi bilan ajralib turadigan muhim elektrofil substratlardir [1]. Ularning tarkibidagi ftor atomlari kuchli induktiv effekti tufayli elektron zichlikni kamaytiradi va karbonil guruhlarning elektrofilikligini oshiradi [6]. Shu sababli, triftoratsetilatseton (TFAH) va geksaftoratsetilatseton (HFAH) kabi ftorlangan β-diketonlar yangi koordinatsion ligandlar yaratishda istiqbolli platforma hisoblanadi [7].

Diaminlar — xususan, 1,3-diaminopropan — karbonil birikmalar bilan kondensatsiya reaksiyasiga kirishib, ikki valentli iminning hosil bo‘lishiga olib keladi. Bunday reaksiyalar orqali hosil bo‘ladigan bis-Schiff asoslari kelat

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komplekslari shakllanishi uchun qulay bo‘lgan bidentat ligandlar sifatida alohida ahamiyatga ega [8,9].

Ligandlarning elektron tuzilishi, donor-aktseptor xususiyatlari va reaksion faolligini baholashda zichlik funksional nazariyasi (DFT) muhim hisoblanadi [2,3]. DFT orqali HOMO–LUMO farqi, elektron zichlik taqsimoti, dipol moment va elektrofilik ko‘rsatkichlar aniqlanadi, bu esa kelajakdagi metall komplekslari barqarorligini tahlil qilish imkonini beradi [5,10].

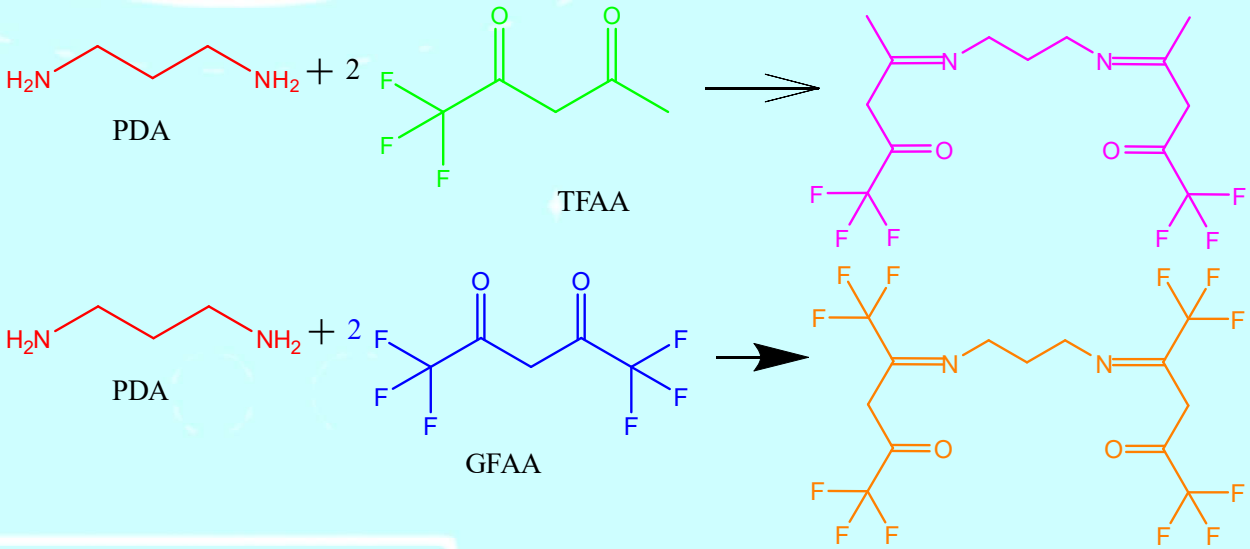
Schiff asoslari bilan funksionallashtirilgan turli matritsalar — jumladan magnit yadrolar — sintezi va ularning qo‘llanilishiga oid masalalar bir qator tadqiqotlarda o‘rganilgan [8-10].

Adabiyotlar tahlili va metodologiya

Ushbu ishda qo‘llanilgan Schiff asosli ligandning sintezi avval chop etilgan metodikaga muvofiq amalga oshirildi [13]. Ligandning elektron tuzilishi va reaktivlik parametrlarini baholashda DFT hisob-kitoblari asosiy rol o‘ynadi [4]. Shu bilan birga, magnit nanostrukturalarga biriktirilgan Schiff bazalarining kompleks hosil qilish xususiyatlari ilgari o‘tkazilgan tadqiqotlar orqali tahlil qilindi [11]. Metodologiyada ishlatilgan barcha kimyoviy moddalar va sharoitlar oldingi tadqiqotlar bilan mos keladi va laboratoriyada xavfsiz sharoitda amalga oshirildi. Bu yondashuv metall komplekslari barqarorligini, struktura-xususiyat bog‘liqligini va potentsial qo‘llanilish sohalarini chuqur o‘rganish imkonini beradi. [5].

Ftorlangan β-diketonlar:Triftoratsetilatseton (TFAA), Geksaftoratsetilatseton (HFAA) **Amin komponent**:1,3-diaminopropan **Reaksiya sharoiti:**Erituvchi: Etanol,Harorat: 20-25 °C,Vaqt: 1-2 soat

Reaksiya tenglamasi



Ajratish: Reaksiya tugagach, aralashma qorong'u joyda bug'latiladi, cho‘kma ajratiladi, sovuq etanol bilan yuviladi va quritiladi.

NATIJA VA MUHOKAMA

Kvant-kimyoviy metodlar

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Hisoblashlar B3LYP/6-31G(d,p) darajasida Gaussian 09 dasturida olib borildi. Mazkur metod organik ligandlar uchun optimal aniqlik va samaradorlik nisbatiga ega bo‘lgan DFT yondashuvlardan biridir [2,3]. Natijalar Avogadro va ChemCraft dasturlari orqali vizuallashtirildi va 1-jadvalda joylashtirildi.[10].

1-jadval

Birikmalarning Kvant Kimyoviy Hisoblashlari energetik parametrlari

Kvant-kimyoviy parameter	1,3-diaminopropan (PDA)	1,1,1-triftor-2,4-pentandion (TFAA)	**1,1,1,5,5,5-geksafluoro-2,4-pentandion**. (GFAA)
E_{HOMO}, eV	-5,78	-7,86	-8,76
E_{LUMO}, eV	-1,13	-2,72	-4,55
$\|\Delta E\| = E_{LUMO} - E_{HOMO}$, (eV)	4,65	5,14	4,21
Ionlanish potensiali, $I = - E_{HOMO}$, (eV)	5,78	7,86	8,76
Elektronga moyillik, $A = - E_{LUMO}$, (eV)	1,13	2,72	4,55
Elektromanfiylik, $\chi = (I + A)/2$ (эВ)	3,455	5,29	6,655
Kimyoviy qattiqlik, $\eta = (I - A)/2$ (eV)	2,325	2,57	2,105
Kimyoviy potensial, $\mu_p = - (I + A)/2$ (eV)	-3,455	-5,29	-6,655
Kimyoviy yumshoqlik, $\sigma = 1/(2\eta)$ (eV^{-1})	0,215	0,195	,0237
Elektrofillik ko‘rsatkichi, $\omega = \mu_p^2/2\eta$ (eV)	2,57	5,44	10,52
Maksimal zaryad uzatish indeksi, ($\Delta Nmax. = -\mu_p/\eta$)	1,486	2,06	3,16
Dipol momenti, μ, (Debay)	2.3700	5.1990	2.3066
Umumiy energiya	-6253.64	-17510.8	-25612

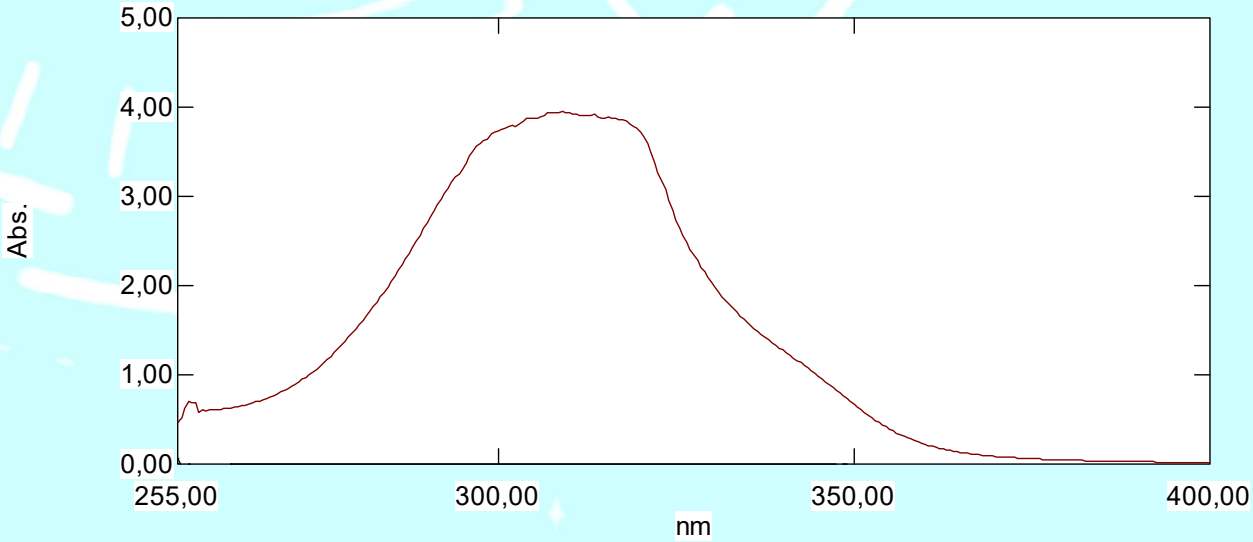
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Geometrik optimizatsiya:Optimallashgan tuzilmalar bukilgan konformatsiyaga ega bo‘lib, metall ionlari bilan kelat hosil qilish uchun qulay holatda ekanligi aniqlandi. Bunday holat Schiff asoslari ligandlari uchun tipik geometrik xususiyatdir [8].

HOMO–LUMO tahlili:Hisoblangan HOMO–LUMO energiya farqlari:TFAH → 5.14 Ev,HFAH → 4.21 Ev,1,3-diaminopropan → 4.65 eV .Kamroq ΔE qiymati *yuqori reaktivlik*dan dalolat beradi, bu esa ftorlangan diketonlardan olingan iminning kuchli elektrofilik tabiatini tasdiqlaydi [5,11].

Elektrofiliklik va kimyoviy qattiqlik**:** Tahlillar shuni ko‘rsatadiki: ΔE qiymatlari ularning reaktivlik darajasi haqida ma’lumot beradi — kichik ΔE bo‘lsa, birikma reaktivroq. HFAH → eng elektrofil birikma (ω = 10.52 eV) . 1,1,1,5,5,5-geksafluoro-2,4-pentandion – eng yuqori elektromanfiylikka ega, eng elektrofilik birikma hisoblanadi.1,3-diaminopropan → eng kuchli nukleofil (χ = 3.455 eV) . 1,3-diaminopropan – eng kichik elektromanfiylik va elektrofiliklikka ega → nisbatan nukleofil xususiyat kuchliroq.Bu AESA (electrophilicity index) nazariyasi bilan mos keladi [5].

Dipol moment: Dipol momentlar molekulalarning qutblanish darajasini ko‘rsatadi, bu esa ularning kelajakdagi metall ionlari bilan o‘zaro ta’sirida muhim rol o‘ynaydi [11]

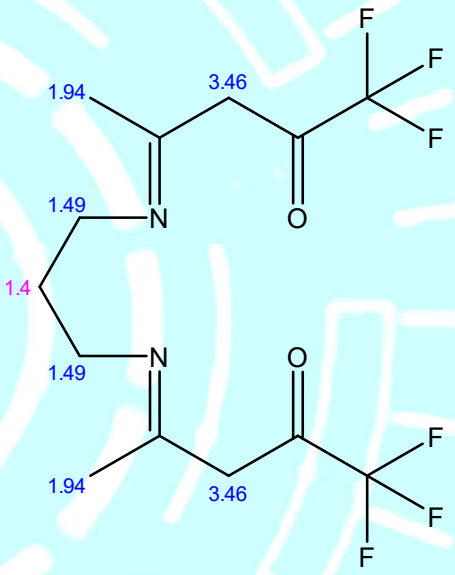


1-rasm UV-spektrning tahlili

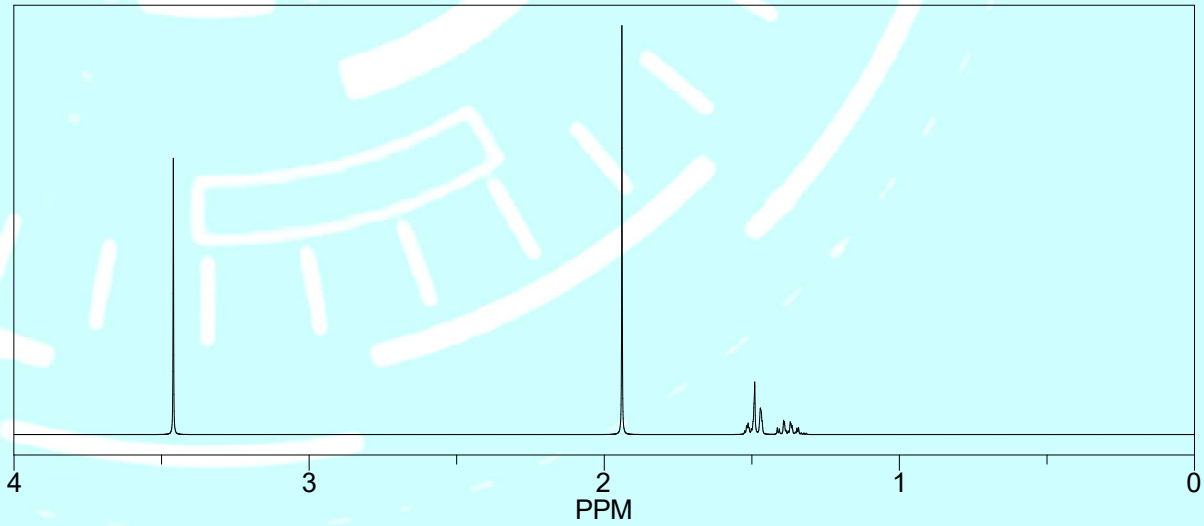
Spektr 255 nm dan 400 nm gacha bo‘lgan UV sohani qamrab olgan.Bu diapazon odatda π→π* yoki n→π* elektron o‘tishlariga tegishli.Spektrda 300–310 nm atrofida keng yutilish maksimumi kuzatilmoqda.Yutilish qiymati (Abs.) ~4.0 atrofida — bu juda kuchli yutilish.Cho‘qqi keng bo‘lib, o‘tishning ko‘p komponentli yoki bir nechta yaqin elektron o‘tishlar bir-biriga qo‘shilib ketganini ko‘rsatadi.Bu ko‘pincha:π–π* o‘tishlar,yoki keto–enol tautomeriyaga ega molekulalarda uchraydi.340 nm dan keyin yutilish tez pasayadi va 380–400 nm oralig‘ida deyarli 0 ga yaqinlashadi.Bu molekulaning ko‘rinadigan (VIS)

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diapazonda yutilmasligini ko‘rsatadi — demak, modda rangsiz yoki engil sariq bo‘lishi mumkin.



2-rasm



3-rasm

3-rasmdagi spektr ^{1}H-YMR (proton NMR) : δ ≈ 3.3–3.5 ppm atrofidagi kuchli singlet

– Bu signal odatda –CH_2– yoki –N–CH_2– guruhlariga mos keladi. Shiff asoslari va diamino-propandan hosil bo‘lgan ligandlarda aminopropan zanjiridagi metilen protonlari aynan shu sohada chiqishi kutiladi.

-δ ≈ 1.6–1.8 ppm atrofidagi signal

– Bu sohada ko‘pincha markaziy –CH_2– (alifatik zanjirning o‘rtasidagi) protonlar chiqadi.1,3-diaminopropan skeletiga xos.

-δ ≈ 0.9–1.2 ppm atrofidagi kichik signallar

– Ehtimoliy qoldiq erituvchi, kuchsiz alifatik protonlar, yoki iz miqdordagi qo‘shimchalar ga tegishli bo‘lishi mumkin.

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Spektrdagi proton signallari 1,3-diaminopropan fragmenti bilan kondensatsiyalangan Shiff asoslari strukturasiga mos keladi.Asosiy protonlar alifatik –CH_2– guruhlaridan iborat bo‘lib, aromatik protonlar yo‘qligi spektrda ko‘rinmayapti yoki ushbu ko‘rinishlarda mavjud emas.

XULOSA

TFAA va HFAA asosida sintez qilingan Schiff ligandlari yuqori elektrofilik xususiyatga ega bo‘lib, kuchli xelat hosil qiluvchi potentsialga ega ekanligi DFT hisoblashlari bilan tasdiqlandi. Ligandlarning ΔE energiya farqlari, elektrofilik indekslari va dipol momentlari ularning metall-kompleks sintezida samarali qo‘llanishi mumkinligini ko‘rsatadi. Bu tadqiqot natijalari kelgusida ftorlangan organik ligandlar asosida barqaror koordinatsion komplekslar yaratish uchun nazariy asos bo‘lib xizmat qiladi.Bu KKH (diagnostik) xulosalarning qanchalik o‘rinli ekanligi keyingi tajriba (eksperimental) tadqiqotlar natijalari bilan solishtirilib tahlil etiladi.

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