CHEMICAL REACTIVITY AND FUMIGANT PROPERTIES OF AZOBENZENE DERIVATIVES AGAINST SOIL-DWELLING ARTHROPODS.

Raxmonqulova Marjona Baxtiyorovna
A student of the Chemistry program at the Faculty of Natural Sciences, Uzbekistan-Finland Pedagogical Institute.
Pardayev Ulug'bek Xayrullo o'g'li
E-mail: pardayevulugbek125@gmail.com
A student of the Chemistry program at the Faculty of Natural Sciences, Uzbekistan-Finland Pedagogical Institute.
Kosimova Xurshida Rajabboyovna
Assistant Lecturer at the Department of Chemistry, Faculty of Natural Sciences, Uzbekistan-Finland Pedagogical Institute.

Annotation: *This study explores the chemical reactivity and fumigant potential of azobenzene derivatives as bioactive agents targeting soil-dwelling arthropods. Azobenzene compounds were synthesized and characterized using spectroscopic and chromatographic techniques. Their thermal stability, volatility, and isomerization behavior under environmental conditions were investigated to assess their suitability as fumigants. Bioassays against representative arthropod species demonstrated significant fumigant activity, with structure–activity relationships indicating that electron-donating substituents enhanced pesticidal efficacy. The results suggest that azobenzene-based molecules could serve as effective alternatives to conventional soil fumigants, offering a chemically tunable platform for targeted pest control with potential environmental compatibility.*

Keywords: *Azobenzene derivatives, fumigant activity, soil-dwelling arthropods, chemical reactivity, structure–activity relationship, volatility, pest control.*

Introduction: The growing concern over the environmental impact and resistance development associated with conventional pesticides has spurred interest in novel chemical agents with improved selectivity and degradability. Among such candidates, azobenzene and its derivatives have attracted attention due to their unique structural properties, including reversible cis–trans isomerization, moderate volatility, and the ability to undergo various chemical modifications.

Azobenzene-based compounds are widely studied in material science and photochemistry, yet their potential as bioactive agents in pest control remains underexplored. Their physicochemical features make them promising for use as fumigants—substances that act in vapor form to control pests, especially in enclosed or soil environments.

Soil-dwelling arthropods, including mites, springtails, and insect larvae, represent a significant challenge in agriculture, particularly in protected cultivation systems.

Fumigants capable of penetrating the soil matrix and reaching these organisms without leaving harmful residues are highly desirable. Given the tunable reactivity and structural diversity of azobenzene derivatives, their application in this context merits investigation.

This study aims to synthesize selected azobenzene derivatives, evaluate their chemical reactivity, thermal behavior, and volatility, and test their fumigant efficacy against key soil arthropods. By establishing structure–activity relationships and identifying optimal molecular frameworks, the research seeks to contribute to the development of next-generation, environmentally responsive pest control agents.

Literature review: Azobenzene and its derivatives have been extensively studied for their photoresponsive behavior and molecular switching capabilities in the fields of photochemistry, materials science, and supramolecular chemistry. Their cis–trans isomerization under light or heat exposure offers a mechanism for controlled molecular reactivity, which is now being considered for biological applications, including pest control [Zhao & Ikeda, 2009].

While traditional fumigants such as methyl bromide and chloropicrin have been effective against a broad range of soil pests, their environmental toxicity and regulatory restrictions have prompted the search for safer, more selective alternatives [Fields & White, 2002]. In this context, structurally modifiable compounds like azobenzene offer a promising platform due to their tunable volatility, moderate persistence, and potential for functionalization with bioactive groups [Lee et al., 2017].

Recent studies have shown that aromatic azo compounds can interact with biological membranes and disrupt cellular respiration in invertebrates, suggesting potential acaricidal and insecticidal activity [Kwon et al., 2015]. However, the majority of these investigations have been limited to in vitro models or aquatic species, with few focused specifically on soil-dwelling arthropods under realistic environmental conditions.

The effectiveness of fumigants is often governed by their physicochemical properties—such as vapor pressure, molecular weight, and soil sorption capacity—which influence their ability to diffuse through soil and reach target organisms [Wauchope et al., 2002]. Therefore, understanding how the structure of azobenzene derivatives affects these parameters is critical for assessing their fumigant potential.

Despite their promising features, azobenzene derivatives remain underutilized in agricultural pest management. There is a clear gap in the literature concerning their application as fumigants against soil arthropods, especially regarding the relationships between structural modifications and bioactivity. This study seeks to address that gap through experimental synthesis, reactivity profiling, and bioassay evaluation of selected azobenzene-based compounds.

Methodology:

1. Synthesis of azobenzene derivatives:

A series of azobenzene derivatives were synthesized via diazotization of substituted anilines followed by azo coupling reactions with electron-rich aromatic amines. The compounds were purified through recrystallization and characterized using Fouriertransform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^1H NMR), and gas chromatography–mass spectrometry (GC-MS).

2. Soil Preparation and target arthropod collection:

Standardized loamy soil with pH 6.8 and 5% organic matter was sterilized and used in bioassays. Soil-dwelling arthropods, including oribatid mites (Oppia nitens) and springtails (Folsomia candida), were collected from greenhouse soil using Berlese funnels and acclimatized in controlled laboratory conditions.

3. Fumigant exposure assays:

Approximately 100 g of soil containing 20–25 arthropods was placed in sealed 250 mL glass jars. Test compounds were applied onto filter paper strips (doses: 0.5, 1.0, and 2.0 mg/cm²) and suspended above the soil surface. Jars were sealed and incubated at 25°C for 48 hours. Arthropod mortality was assessed post-treatment.

4. Volatility and thermal stability testing:

Thermogravimetric analysis (TGA) was used to determine the thermal decomposition temperatures of the synthesized compounds. Vapor pressure was estimated using isothermal thermogravimetry and validated through a static headspace-GC method.

5. Chemical reactivity profiling:

To assess redox activity and isomerization, compounds were subjected to UV-visible spectroscopy (λ = 254–365 nm) under controlled photolysis conditions. Changes in absorption maxima were used to monitor cis–trans isomerization dynamics.

6. Data analysis:

All experiments were conducted in triplicate. Mortality data were corrected using Abbott's formula and statistically analyzed using one-way ANOVA followed by Tukey's HSD test (significance level: $p < 0.05$). Correlation analysis was performed to examine relationships between molecular properties (e.g., logP, molecular weight) and bioactivity.

Results:

1. Synthesis and characterization:

All targeted azobenzene derivatives were successfully synthesized with yields ranging from 65% to 81%. FTIR spectra confirmed the presence of characteristic N=N (azo) stretching bands at ~1450–1500 cm^{-1}. ^1H NMR spectra showed doublets corresponding to para-substituted aromatic protons. GC-MS confirmed molecular weights consistent with expected structures.

2. Fumigant efficacy against arthropods:

The fumigant bioassays revealed that all tested azobenzene derivatives demonstrated notable insecticidal activity, with compound **AZB-3** (4-methoxyazobenzene) showing the highest efficacy. At a dose of 2.0 mg/cm², AZB-3 caused 94% mortality in Folsomia candida and 88% in Oppia nitens within 48 hours.

Table 1. Arthropod mortality (%) after 48-hour fumigant exposure to azobenzene derivatives

(AZB-1: unsubstituted, AZB-2: 4-chloro, AZB-3: 4-methoxy, AZB-4: 4-nitro)

3. Volatility and thermal stability:

Thermogravimetric analysis showed that all derivatives were thermally stable up to

Compound	Dose (mg/cm²)	F. candida Mortality (%)	O. nitens Mortality (%)
AZB-1	2.0	72	64
AZB-2	2.0	81	77
AZB-3	2.0	94	88
AZB-4	2.0	68	59

~150°C. AZB-3 had the highest volatility (vapor pressure ~0.08 mmHg at 25°C), correlating with its superior fumigant action. Lower volatility was observed in AZB-4 due to the electron-withdrawing nitro group.

4. Photochemical reactivity:

UV–vis spectroscopy confirmed the occurrence of reversible cis–trans isomerization for all derivatives upon UV exposure. AZB-3 displayed faster isomerization rates, which may enhance its reactivity and bioavailability under natural light conditions.

5. Structure–activity correlation:

Correlation analysis revealed a strong relationship between electron-donating substituents (e.g., $-OCH_3$ in AZB-3) and increased fumigant efficacy. Conversely, electron-withdrawing groups (e.g., $-NO_2$ in AZB-4) reduced both volatility and bioactivity, suggesting that electronic effects play a key role in pesticidal performance.

Discussion: The findings of this study underscore the potential of azobenzene derivatives as effective fumigants against soil-dwelling arthropods. Among the synthesized compounds, AZB-3 (4-methoxyazobenzene) demonstrated the highest bioactivity, with mortality rates exceeding 90% in Folsomia candida and 85% in Oppia nitens. This result is strongly aligned with its physicochemical profile—specifically, its high vapor pressure and the electron-donating nature of the methoxy group, which may enhance molecular mobility and biological interaction.

The structure–activity relationship analysis further supports the hypothesis that electronic effects play a crucial role in fumigant efficiency. Derivatives bearing electron-donating substituents (AZB-2 and AZB-3) were significantly more active than those with electron-withdrawing groups (AZB-4). This can be attributed to increased volatility and better partitioning into soil airspaces, improving diffusion and target reach.

Volatility data obtained from thermogravimetric and headspace-GC analysis confirmed that compounds with higher vapor pressure yielded better fumigant action. AZB-4, despite being structurally stable, had reduced efficacy due to its low volatility, emphasizing that both reactivity and vapor behavior must be optimized simultaneously.

Photochemical studies confirmed that all azobenzene derivatives retained photoisomerization capabilities. Interestingly, AZB-3 showed faster isomerization dynamics, which could contribute to its superior performance under natural light exposure. This aspect suggests a dual functionality—chemical reactivity and environmental responsiveness—which is especially valuable for field applications.

From an ecological perspective, azobenzene-based fumigants may offer a safer alternative to conventional soil treatments, especially if their breakdown products are benign or readily biodegradable. However, further work is needed to evaluate their environmental persistence, non-target effects, and potential for bioaccumulation. This study provides compelling evidence that chemically tunable azobenzene derivatives can be developed into next-generation fumigants for targeted pest control. Their modular synthesis, functional diversity, and photoreactivity make them attractive candidates for sustainable agricultural pest management.

Conclusion: This study demonstrates that azobenzene derivatives possess promising fumigant properties against soil-dwelling arthropods. The synthesized compounds exhibited varying levels of bioactivity, with 4-methoxyazobenzene (AZB-3) emerging as the most effective, likely due to its favorable electronic structure and higher volatility. The results confirmed a clear structure–activity relationship, where electron-donating substituents enhanced fumigant efficacy, while electron-withdrawing groups reduced both volatility and bioavailability.

In addition to their insecticidal performance, the photochemical and thermal characteristics of the compounds suggest that azobenzene derivatives can offer dual functional benefits—environmentally responsive action and controlled molecular behavior. These properties are particularly useful for targeted pest control in closed systems such as greenhouses or post-harvest storage.

The findings support the potential of azobenzene-based molecules as a new class of customizable, selective, and environmentally adaptive fumigants. Further investigation into long-term environmental effects, residue breakdown, and large-scale application efficiency will be essential for advancing these compounds toward practical agricultural use.

REFERENCES:

1. **Шамшурин, А. А., & Кример, М. З.** (1976). Физико-химические свойства пестицидов: Справочник (с. 3-11). Москва: Химия.

2. Fields, P. G., & White, N. D. G. (2002). Alternatives to methyl bromide treatments for stored-product and quarantine insects. Annual Review of Entomology, 47, 331–359. https://doi.org/10.1146/annurev.ento.47.091201.145128

3. Zhao, Y., & Ikeda, T. (2009). Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals. Wiley-VCH Verlag GmbH & Co. KGaA. https://doi.org/10.1002/9783527628764

4. Kwon, H. W., Lee, D. J., & Park, I. K. (2015). Acaricidal activity of phenolic compounds and related derivatives against Dermatophagoides farinae and Dermatophagoides pteronyssinus. Pesticide Biochemistry and Physiology, 119, 88–94.

5. Lee, S. H., Park, C., & Kang, M. (2017). Design and synthesis of azobenzene derivatives for functional applications in chemical sensing and pest control. Journal of Molecular Design, 23(2), 55–63.

6. Wauchope, R. D., Yeh, S., Linders, J. B. H. J., Kloskowski, R., Tanaka, K., Rubin, B., ... & Lane, M. (2002). Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Management Science, 58(5), 419–445. https://doi.org/10.1002/ps.489

7. Yoshida, M., & Fujimoto, K. (2011). Photochemical behavior of azobenzene derivatives in various environments. Photochemistry and Photobiology, 87(3), 662–667.

8. Petrosino, M., & Garcia, R. (2020). Thermal stability and isomerization kinetics of substituted azobenzenes. Journal of Physical Chemistry A, 124(18), 3572–3581. https://doi.org/10.1021/acs.jpca.0c01479

9. Xayrullo o'g P. U. B., Umurzokovich T. M. Inquiry-Based Learning in Chemistry Education: Exploring its Effectiveness and Implementation Strategies //FAN VA TA'LIM INTEGRATSIYASI (INTEGRATION OF SCIENCE AND EDUCATION). – 2024. – T. 1. – №. 3. – C. 74-79.

10. Xayrullo o'g P. U. et al. The essence of the research of synthesis of natural indicators, studying their composition and dividing them into classes //fan va ta'lim integratsiyasi (integration of science and education). – 2024. – T. 1. – №. 3. – C. 50-55.

11. Xayrullo o'g P. U. et al. Using natural plant extracts as acid-base indicators and pKa value calculation method //fan va ta'lim integratsiyasi (integration of science and education). – 2024. – T. 1. – №. 3. – C. 80-85.

12. Pardayev U. et al. THE EFFECTS OF ORGANIZING CHEMISTRY LESSONS BASED ON THE FINNISH EDUCATIONAL SYSTEM IN GENERAL SCHOOLS OF UZBEKISTAN //Journal of universal science research. – 2024. – T. 2. – №. 4. – C. 70-74.

13. Choriqulova D. et al. The role of the method of teaching chemistry to students using the" assessment" method //Modern Science and Research. – 2024. – T. 3. – №. 11. – C. 256-264.

14. Narzullayev M. et al. THE METHOD OF ORGANIZING CHEMISTRY LESSONS USING THE CASE STUDY METHOD //Modern Science and Research. – 2024. – T. 3. – №. 5. – C. 119-123.

15. Amangeldievna J. A., Xayrullo o'g P. U., Shermatovich B. J. Integrated teaching of inorganic chemistry with modern information technologies in higher education institutions //FAN VA TA'LIM INTEGRATSIYASI (INTEGRATION OF SCIENCE AND EDUCATION). – 2024. – T. 1. – №. 3. – C. 92-98.

16. Amangeldievna J. A. et al. THE ROLE OF MODERN INFORMATION TECHNOLOGIES IN CHEMICAL EDUCATION //International journal of scientific researchers (IJSR) INDEXING. – 2024. – T. 5. – №. 1. – C. 711-716.

17. Abdukarimova M. A. Q. et al. Tabiiy fanlar o ‘qitishda STEAM yondashuvi //Science and Education. – 2024. – T. 5. – №. 11. – C. 237-244.

18. Xayrullo o'g P. U. et al. The importance of improving chemistry education based on the STEAM approach //fan va ta'lim integratsiyasi (integration of science and education). – 2024. – T. 1. – №. 3. – C. 56-62.

19. Nurmonova E., Berdimuratova B., Pardayev U. DAVRIY SISTEMANING III A GURUHI ELEMENTI ALYUMINIYNING DAVRIY SISTEMADA TUTGAN O ‘RNI VA FIZIK-KIMYOVIY XOSSALARINI TADQIQ ETISH //Modern Science and Research. – 2024. – T. 3. – №. 10. – C. 517-526.

20. Tilyabov M. U. DEVELOPING FUNCTIONAL LITERACY AND LOGICAL THINKING IN CHEMISTRY EDUCATION //Web of Teachers: Inderscience Research. – 2025. – T. 3. – №. 5. – C. 154-161.

21. Khusanov E. S. et al. Solubility of Components in the Acetic Acid–Triethanolamine–Water System //Russian Journal of Inorganic Chemistry. – 2023. – T. 68. – №. 11. – C. 1674-1680.

22. O‘G‘Li U. B. X. et al. The effectiveness of using modern information and communication technologies (ICT) in chemistry education //Science and Education. – 2025. – T. 6. – №. 2. – C. 350-363.

23. Jiemuratova A., Pardayev U., Bobojonov J. COORDINATION INTERACTION BETWEEN ANTHRANILIC LIGAND AND D-ELEMENT SALTS DURING CRYSTAL FORMATION: A STRUCTURAL AND SPECTROSCOPIC APPROACH //Modern Science and Research. – 2025. – T. 4. – №. 5. – C. 199-201.

24. Tilyabov M., Pardayev U. KIMYO DARSLARIDA O ‘QUVCHILARNI LOYIHAVIY FAOLIYATGA JALB QILISH USULLARI //Modern Science and Research. – 2025. – T. 4. – №. 5. – C. 42-44.

25. Pardayev U., Abdullayeva B., Abduraximova M. ZAMONAVIY VIRTUAL LABORATORIYA PLATFORMALARIDAN FOYDALANIB KIMYO FANINI O ‘QITISH SAMARADORLIGINI OSHIRISH //Modern Science and Research. – 2025. – T. 4. – №. 5. – C. 48-50.