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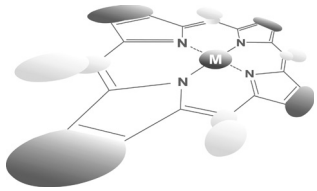


# Microwave-assisted synthesis and sublimation enthalpies of hemiporphyrazines

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**ABSTRACT:** It was established that microwave irradiation solvent-free processing of 2,6-diaminopyridine or 1,3-phenylenediamine with phthalonitrile or 4-*tert*-butylphthalonitrile led to corresponding hemiporphyrazines with sufficiently high yields and a huge reduction in the time required for synthesis, from 8–12 h to 20 min. The data of IR and UV-vis spectroscopies and elemental analysis of the final products were found to be similar to those described in literature. The obtained hemiporphyrazines were characterized by $^{1}$H and $^{13}$C NMR data. We applied the Knudsen effusion method with mass spectrometric control of vapor composition. The mass spectrometric investigations established that the macrocyclic compounds give a stable stream of particles and their enthalpies of sublimation were estimated by the second law of thermodynamics.

**KEYWORDS:** hemiporphyrazine, carbahemiporphyrazine, microwave-assisted synthesis, sublimation enthalpy.



## INTRODUCTION

Since their discovery [1], hemiporphyrazines [2] (Hps) have been attracting steady scientific and practical interest [3–6]. They can be considered as derivatives of phthalocyanine (Pc) [7] where two opposite-faced isoindole rings (B) are replaced by rests of aromatic diamines (A) in order to form an ABAB-type macrocyclic system. This structural modification interrupts the conjugation in the inner aromatic macrosystem which is characteristic of blue-colored phthalocyanines and leads to hypsochromically shifted yellow-orange Hps [8]. Various aspects of geometry and electron structure and relationship "structure-properties" of Hps are the objectives of manifold detailed studies [9–12]. Hemiporphyrazines are demonstrated to be a good platform for structural modifications to both central core and periphery of the macrocycles [13–18] that allows for fine tuning of their properties. Thus Hps and their metallocomplexes reveal various practically useful properties [19–24] and are of special interest as optical limiters [25, 26] and excitonic luminescence [27], nonlinear optical and photoelectronic materials [28–30].

The general method of synthesizing of hemiporphyrazines is a crossover-condensation of phthalonitrile or its derivatives with carbo- or heterocyclic diamines [1, 2, 9, 13, 23]. The protons donating organic solvents, such as butyl alcohol, ethoxy ethanol, ethylene glycol, phenol and others, are used for this purpose. As a rule, a complicated mixture of various products results in separation of the main products from the reaction mixture that seems to be a tedious task. Thus, solvents

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used for synthesis, long duration of heating (8–12 h) and multistep purification of target compounds are the main difficulties of these approaches.

Alternatively, microwave initialization seems to be an effective approach that reduces the number of difficulties. The effectiveness of microwave-assisted synthesis for various fields of organic chemistry has been recently reviewed [31, 32]. The main reasons to use microwave initialization are a huge shortening of reaction duration and the possibility of using a solvent-free protocol that improves safety aspects and could be viewed as a green chemistry approach.

Successful applications of microwave irradiation (MWI) in porphyrins and phthalocyanines chemistry have been reported in a number of works [33–37]. However, to the best of our knowledge, an application of microwave irradiation to preparation of Hps has not yet appeared in the literature.

Initially, sublimation in vacuum for purification of hemiporphyrazines and their metal complexes was described in pioneering works dedicated to the synthesis of Hps [1, 38]. Later this method was developed [39] and applied to deposition of tin layers upon surfaces in order to study electro- and photophysical properties of Hps. Despite their large applicability, the quantitative characteristics of their sublimation ability remain unknown.

Therefore, the target of this work is to study the principal applicability of microwave irradiation to the synthesis of hemiporphyrazine, carbahemiporphyrazine and their *tert*-butyl analogs and to provide quantitative estimation of their enthalpies of sublimation.

## EXPERIMENTAL

### Materials and methods

2,6-Diaminopyridine (**1**) and 1,3-phenylenediamine (**2**) were purified by recrystallization from dichloromethane and dried under reduced pressure at 60 °C for 4 h. Phthalonitrile (**3**) was purified by recrystallization from acetone and dried under reduced pressure at 60 °C for 4 h. 4-*tert*-Butylphthalonitrile (**4**) was prepared following the method described in the literature [40]. Column chromatography was conducted on silica gel (Merck-60). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide 60 $F_{254}$ (Merck). Melting points were recorded on a JiaHang Instruments apparatus in open capillary tubes. MALDI-TOF spectra were obtained with Shimadzu Biotech Axima Confidence in using a positive ion field without matrix. The test for carbon, nitrogen and hydrogen was carried out with a FlashEA 1112 CHNS–O Analyzer. UV-vis spectra were recorded on a HITACHI U-2001 at room temperature in quartz cuvettes ($l$ = 10 mm). IR spectra were recorded on an Avatar 360 FT-IR spectrometer. NMR spectra were recorded on an Avance III Bruker 500 NMR spectrometer in DMSO-$D_6$ or $CDCl_3$ with operating frequencies of protons of 500 MHz and on carbon 126 MHz. Chemical shifts are expressed in parts per million (ppm), and coupling constants ($J$) in Hertz (Hz). All reactions were performed using CEM-Discover monomode equipment with systems of continuous supply of microwave radiation (the power supply was set by an operator in a range of 0–300 W) and magnetron frequency 2455 MHz in open vessels under solvent-free conditions. Temperatures in the range 25–250 °C, evaluated by infrared detection, were maintained constant throughout the reaction by modulation of emitted MW power. The mass spectrometric study of the process of sublimation of **5**–**8** by the Knudsen method was carried out using a MI-1201 commercial magnetic sector mass spectrometer modified for thermodynamic studies. The solid sample was evaporated from a stainless steel effusion cell. The ratio of the cross-section area of the cell to the effusion aperture area was about 1000. The cell temperature was measured by a tungsten-rhenium thermocouple W-Re 5/20. Mass spectra were recorded in vacuum no more than $10^{-7}$ Torr and at an ionization energy of 36 eV for **5** ($C_{26}N_8H_{16}$) and **8** ($C_{36}N_6H_{34}$); 39 eV for **7** ($C_{34}N_8H_{32}$) and 50 eV for **6** ($C_{28}N_6H_{18}$). Accelerating voltage was 5 kV for all compounds. Cathode emission current was $I_{emis}$ = 0.5 mA. The mass spectra were recorded in vapor temperature ranges of 469–531 K (**5**), 464–525 K (**6**), 486–516 K (**7**) and 441–481 K (**8**). The mass spectrometric investigations established that all compounds give a stable stream of particles. All four mass spectra show high-intensity lines for molecular ions. No ions corresponding to oligomeric species were detected.

### Synthesis

***General procedure.*** A mixture of equimolecular quantities of 2,6-diaminopyridine (**1**) or 1,3-phenylenediamine (**2**) and phthalonitrile (**3**) or *tert*-butylphthalonitrile (**4**) was fine-milled in an agate pounder and heated at 150 °C for 20 min in a focused-microwave oven with dynamic power not more than 100 W in open vessels with the solvent-free protocol. After purification, selected with respect of the solubility and as described below, the substances **5**–**8** were finally dried under reduced pressure at 130 °C for 4 h.

**5,26:13,18-*Diimino*-7,11:20,24-*dinitrilo*-[*c,n*]-*dibenzo*-1,6,12,17-*tetraazacyclodocosene*-[1,3,5,7,9,-12,14,16,21,23]-*decene* (5)** was synthesized following the general procedure by interaction of 0.12 g (0.93 mmol) phthalonitrile and 0.1 g (0.93 mmol) 2,6-diaminopyridine. The low-molecular products were isolated by column chromatography on silica gel (ethyl acetate:hexane = 3:1) and the target product was obtained by recrystallization from benzyl alcohol. Final drying in vacuum resulted in an orange product with yield 0.06 g, 29% (38% [1]). Melting point: 346–347 °C (344 °C [1]). UV-vis, $\lambda_{max}$, *nm* (log$\varepsilon$), (DMF): 352 (4.22) (354 (4.31) [1]). IR (KBr): $\nu$, $cm^{-1}$:

690, 771, 1099, 1152, 1231, 1430, 1471, 1555, 1577, 1666, 3450. Found: C, 70.0; H, 3.6; N, 25.0%; molecular formula $C_{26}H_{16}N_8$ requires C, 70.9; H, 3.7; N, 25.4%. $^1$H NMR (500 MHz, DMSO) δ (ppm): 10.74 (s, 2H), 8.00–7.96 (m, 4H), 7.82 (t, $J$ = 7.8 Hz, 2H), 7.80–7.76 (m, 4H), 6.85 (d, $J$ = 7.9 Hz, 4H). $^{13}$C NMR (126 MHz, DMSO) δ (ppm): 160.17 (s), 151.86 (s), 140.42 (s), 135.07 (s), 132.89 (s), 122.70 (s), 114.73 (s). MALDI-TOF m/z, Da: found: 441.1, calculate for $C_{26}H_{17}N_8^+$: EM = 441.1 $[M + H]^+$. $\Delta H°_s$ = 191(1) kJ/mol.

**5,26:13,18-*Diimino*-7,11:20,24-*dimetheno*-[*c,n*]-*dibenzo*-1,6,12,17-*tetraazacyclodocosene*-[1,3,5,7,9,12,-14,16,21,23]-*decene* (6)** was synthesized following the general procedure by interaction of 0.12 g (0.93 mmol) phthalonitrile and 0.1 g (0.93 mmol) *m*-phenylenediamine. The crude product was purified by recrystallization from ethanol. Final drying in vacuum resulted in a yellow product with yield 0.09 g, 45% (71% [38]). Melting point: 379–380 °C (380 °C [38]). UV-vis, $\lambda_{max}$, nm (logε), (DMF): 327 (4.25), 340 (4.08) (328 (4.23), 343 (4.23) [38]). IR (KBr): ν, cm$^{-1}$: 691, 791, 1102, 1261, 1515, 1650, 3441. Found: C, 73.2; H, 4.7; N, 18.5%; molecular formula $C_{28}H_{18}N_6 \cdot H_2O$ requires C, 73.7; H, 4.4; N, 18.4%. $^1$H NMR (500 MHz, DMSO) δ (ppm): 10.39 (s, 2H), 7.99–7.94 (m, 4H), 7.76–7.74 (m, 4H), 7.34 (t, $J_3$ = 7.8Hz, 2H), 6.95 (t, $J_4$ = 1.9 Hz, 2H), 6.78 (dd, $J_3$ = 7.9 $J_4$ = 2.0 Hz, 4H). $^{13}$C NMR (126 MHz, DMSO) δ (ppm): 151.63 (s), 150.10 (s), 135.21 (s), 132.36 (s), 130.48 (s), 122.52 (s), 118.64 (s), 113.97 (s). MALDI-TOF m/z, Da: found: 439.2, 461.1, 477.1, calculate for $C_{28}H_{19}N_6^+$: EM = 439.2 $[M + H]^+$, EM = 461.1 $[M + Na]^+$, EM = 477.1 $[M + K]^+$. $\Delta H°_s$ = 189 (3) kJ/mol.

**2,15(16)-*Di*(*tert-butyl*)-5,26:13,18-*diimino*-7,11:20,24-*dinitrilo*-[*c,n*]-*dibenzo*-1,6,12,17-*tetraazacyclodocosene*-[1,3,5,7,9,12,14,16,21,23]-*decene* (7)** was synthesized following the general procedure by interaction of 0.17 g (0.93 mmol) 4-*tert*-butylphthalonitrile and 0.1 g (0.93 mmol) 2,6-diaminopyridine. The crude product was washed with hot hexane and purified by column chromatography on silica gel (ethyl acetate: hexane = 6:1). Final drying at reduce pressure resulted in a yellow powder with yield 0.03 g, 13%. Melting point: 276–278 °C. UV-vis, $\lambda_{max}$, nm ($CHCl_3$): 358 ($c$ = 4.3 × 10$^{-5}$ M, D = 1.32). IR (KBr): ν, cm$^{-1}$: 678, 692, 800, 873, 956, 998, 1093, 1122, 1254, 1353, 1432, 1482, 1516, 1577, 1599, 1664, 2860, 2957, 3059, 3410. Found: C, 67.4; H, 6.5; N, 18.5%; molecular formula $C_{34}H_{32}N_8 \cdot 3H_2O$ requires C, 67.3; H, 6.3; N, 18.5%. $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.12 (s, 2H), 8.08 (d, $J_4$ = 1.5 Hz, 2H), 7.97 (d, $J_3$ = 8.1 Hz, 2H), 7.76 (d, $J_3$ = 8.1, 2H), 7.40 (t, $J_3$ = 7.8Hz, 2H), 6.88 (m, 4H), 1.23 (s, 18H). MALDI-TOF m/z, Da: found: 553.3, 575.3; calculate for $C_{34}H_{33}N_8^+$: EM = 553.3 $[M + H]^+$; EM = 575.3 $[M + Na]^+$. $\Delta H°_s$ = 214(5) kJ/mol.

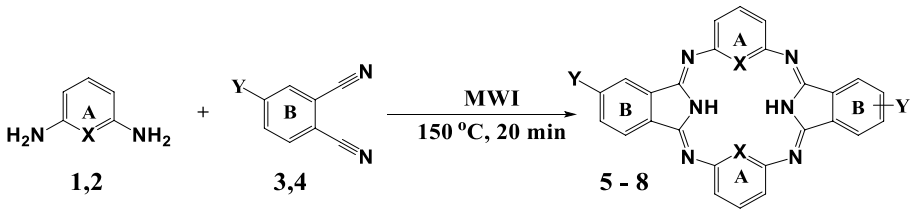
**2,15(16)-*Di*(*tert-butyl*)-5,26:13,18-*diimino*-7,11:20,24-*dimetheno*-[*c,n*]-*dibenzo*-1,6,12,17-*tetraazacyclodocosene*-[1,3,5,7,9,12,14,16,21,23]-*decene* (8)** was synthesized following the general procedure by interaction of 0.17 g (0.93 mmol) 4-*tert*-butylphthalonitrile and 0.1 g (0.93 mmol) *m*-phenylenediamine. The crude product was purified by column chromatography on silica gel (benzene:acetone = 1:1) with subsequent recrystallization from ethanol. Final drying at reduced pressure resulted in yellow powder with yield 0.14 g, 56% (62% [42]). Melting point: 238–240 °C (235–237°, °C [42]). UV-vis, $\lambda_{max}$, nm ($CHCl_3$): 334 ($c$ = 5.73 × 10$^{-5}$ M, D = 1.23) (339 [42]). IR (KBr): ν, cm$^{-1}$: 688, 796, 843, 959, 1046, 1127, 1208, 1258, 1358, 1483, 1521, 1580, 1667, 2869, 2961, 3059, 3274, 3410. Found: C, 75.9; H, 6.4; N, 14.6%; molecular formula $C_{36}H_{34}N_6 \bullet H_2O$ requires C, 76.0; H, 6.4; N, 14.8%. $^1$H NMR (500 MHz, DMSO) δ (ppm): 10.31 (s, 2H), 7.92 (d, $J_4$ = 1.6 Hz, 2H), 7.89 (d, $J_3$ = 8.1 Hz, 2H), 7.80 (dd, $J_3$ = 8.1 Hz, $J_4$ = 1.7 Hz, 2H), 7.33 (tt, $J_3$ = 7.8 Hz, $J_5$ = 2.0 Hz, 2H), 6.87 (m, 2H), 6.76 (m, 4H), 1.39 (s, 18H). $^{13}$C NMR (126 MHz, DMSO) δ (ppm): 155.75 (s), 151.86 (s), 151.53 (s), 150.14 (d, J = 4.3 Hz), 135.25 (s), 132.80 (s), 130.47 (s), 129.76 (s), 122.34 (s), 118.77 (s), 118.57 (d, $J$ = 7.6 Hz), 113.92 (s), 35.66 (s), 31.53 (s). MALDI-TOF m/z, Da: found: 551.3, 573.3, 589.3; calculate for $C_{36}H_{35}N_6^+$: EM = 551.3 $[M + H]^+$; EM = 573.3 $[M + Na]^+$; EM = 589.2 $[M + K]^+$. $\Delta H°_s$ = 178(4) kJ/mol.

## DISCUSSION

At the first stage the influence of temperature upon the reaction run was studied under the following experimental conditions: fine-milled equimolecular mixtures of **1** and **4** were treated in open vessels in a focused-microwave oven without solvent for 20 min within a temperature range from 100 °C to 200 °C. It was observed that when the temperature of the synthesis was conducted below 130 °C, no macroheterocyclic system was detected in the reaction mixtures by MALDI-TOF mass spectrometry. When the temperature reached 150 °C, the formation of hemiporphyrazine was clearly observed. Subsequent increases in temperature led to high molecular product formation. Hence, corresponding hemiporphyrazines **5**–**8** were synthesized at 150 °C for 20 min by crossover-condensation of corresponding diamines **1** and **2** with nonsubstituted **3** and *tert*-butylsubstituted **4** phthalonitriles under microwave irradiation (Scheme 1).

After individual purification selected with respect to the solubility and as described in the experimental section, substances **5**–**8** were finally dried under reduced pressure at 130 °C for 4 h. Data of IR and UV-vis spectroscopies and elemental analysis of the final products **5**–**8** were found to be similar to those described in the literature for corresponding Hps [1, 38, 41, 42] and the characterization of these compounds was completed with mass spectrometry data (Table 1).

It is worth noting that no corresponding phthalocyanines were detected in microwave-assisted synthesis at the




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **X** | N | CH | – | – | N | CH | N | CH |
| **Y** | – | – | H | *t*Bu | H | H | *t*Bu | *t*Bu |

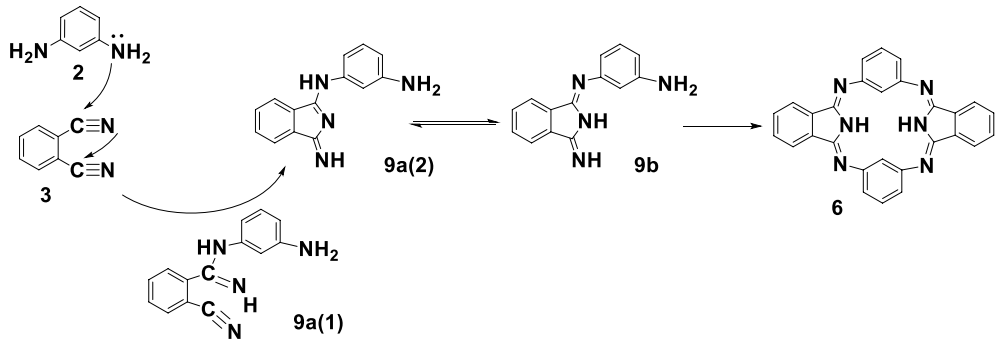
**Scheme. 1.**

**Table 1.** Synthesis duration, yields, melting points, UV-vis and elemental analysis data of **5**–**8** obtained by microwave-assisted synthesis and selected data of corresponding hemiporphyrazines synthesized in organic solvents

| № | Microwave assisted synthesis (solvent-free protocol, heating at 150 °C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $\tau_{synth}$, min | η, % | mp, °C | $\lambda_{max}$ (logε), nm solvent | EM (without matrix), Da<br>Found, Da<br>Calculate, Da | Found, %<br>Calculate, % | | |
| | | | | | | C | N | H |
| **5** | 20 | 29 | 346–347 | 352 (4.22)<br>DMF | 441.1<br>441.1<br>$[M + H]^+$ | $C_{26}H_{16}N_8$ | | |
| | | | | | | 70.0<br>70.9 | 25.0<br>25.4 | 3.6<br>3.7 |
| **6** | 20 | 45 | 379–380 | 327 (4.25), 340 (4.08)<br>DMF | 439.2<br>439.2<br>$[M + H]^+$ | $C_{28}H_{18}N_6 \cdot H_2O$ | | |
| | | | | | | 73.2<br>73.7 | 18.5<br>18.4 | 4.7<br>4.4 |
| **7** | 20 | 13 | 276–278 | 358<br>Chloroform | 553.3<br>553.3<br>$[M + H]^+$ | $C_{34}H_{32}N_8 \cdot 3H_2O$ | | |
| | | | | | | 67.4<br>67.3 | 18.5<br>18.5 | 6.5<br>6.3 |
| **8** | 20 | 56 | 238–240 | 334<br>Hexane | 551.3<br>551.3<br>$[M + H]^+$ | $C_{36}H_{34}N_6 \cdot H_2O$ | | |
| | | | | | | 75.9<br>76.0 | 14.6<br>14.8 | 6.4<br>6.4 |
| | Classical methodic (in boiling butanol) | | | | | | | |
| | $\tau_{synth}$, min | η,% | mp, °C | $\lambda_{max}$ (logε), nm solvent | Lit. | | | |
| **5** | 480 | 38 | 344 | 354 (4.31)<br>DMF | [1] | | | |
| **6** | 1020 | 71 | 380 | 328 (4.23), 343 (4.23)<br>DMF | [38] | | | |
| **7** | 900 | 60 | — | 373<br>EtOH | [41] | | | |
| **8** | 720 | 62 | 235–237 | 333<br>Hexane | [42] | | | |

temperature equal to 150 °C based on both nonsubstituted **3** and *tert*-butylsubstituted **4** phthalonitriles. This fact can be explained by an initial attack of amino group of diamine toward carbon atom of one of the cyano groups of phthalonitrile which is transformed into dimer **9b** *via* intermediate **9a** (Scheme 2). The dimerization of two-unit intermediate **9b** leads to the hemiporphyrazine macrocycle. (The) A similar mechanism was described in the literature [14, 43, 44].

Microwave irradiation in the Hps synthesis illustrated two improvements. First, the time of the synthesis was reduced drastically from 8–10 h to 20 min. The second




**Scheme. 2.**

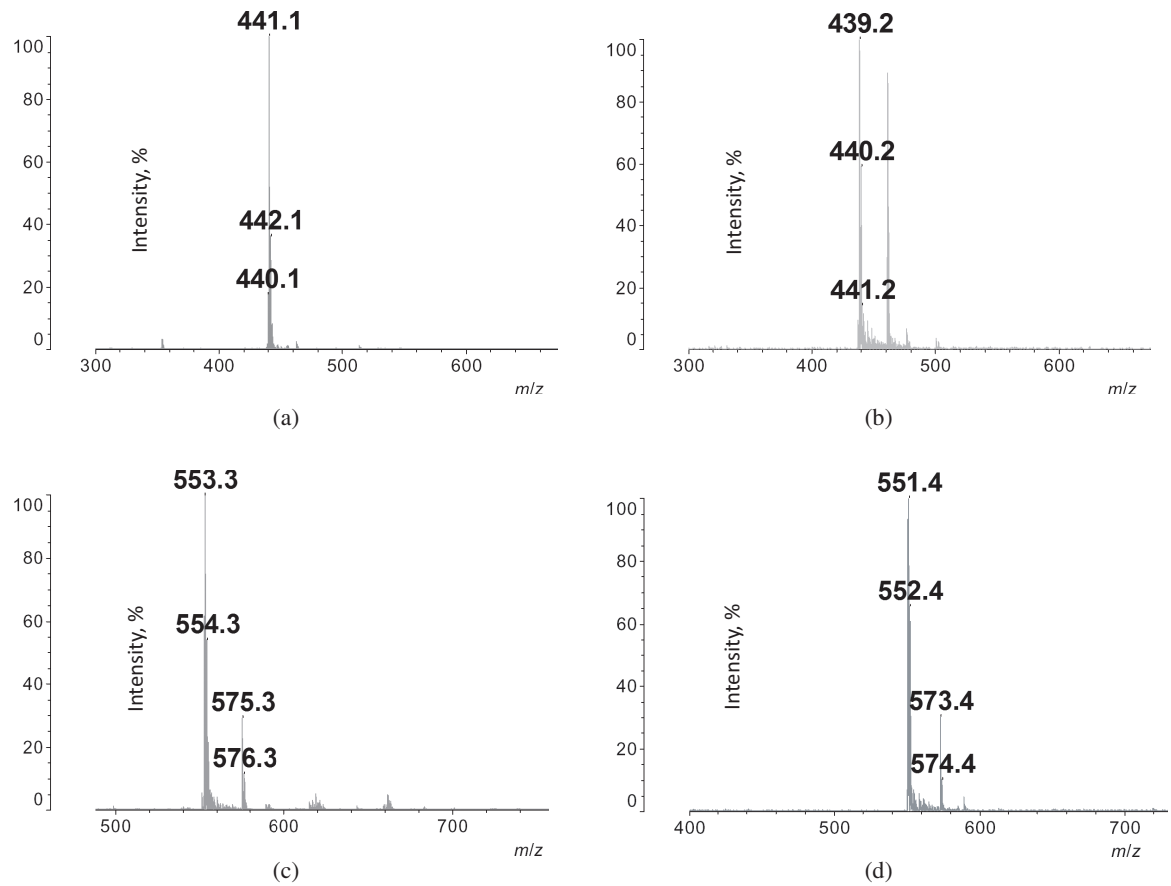



**Fig. 1.** MALDI-TOF mass spectra without matrix of **5** (a), **6** (b), **7** (c) and **8** (d)

improvement involved the elimination of a solvent during the synthesis.

In the case of **1** a large number of byproducts (starting materials, intermediates and various products of condensation) along with Hps **5** and **7** were detected by MALDI-TOF of the reaction mass. The usage of *m*-phenylenediamine **2** led to obtaining of **6** and **8** with moderate yields.

Along with the main signals which correspond to $[M + H]^+$ ions, the signals of $[M + Na]^+$ and $[M + K]^+$ ions were detected in MALDI-TOF (Fig. 1). Good conformity between the calculated isotopic distributions and those derived from experimental data proves this assignment.

It was earlier established that hemiporphyrazines can be sublimated under vacuum [1, 32], but thermodynamic characteristics of these processes have not been reported yet. The mass spectrometric studies performed in the connection with a sublimation process show that **5**–**8** give stable streams of particles at a range of temperatures T = 441–531 K. In all four cases the dependences $ln(I \cdot T) = f(1000/T)$ (Fig. 2) were found to be close to straight lines (the correlation coefficient was 0.999 in all four cases), which is usually observed for the vaporization in the present temperature range without changes of aggregate state of solid phase.

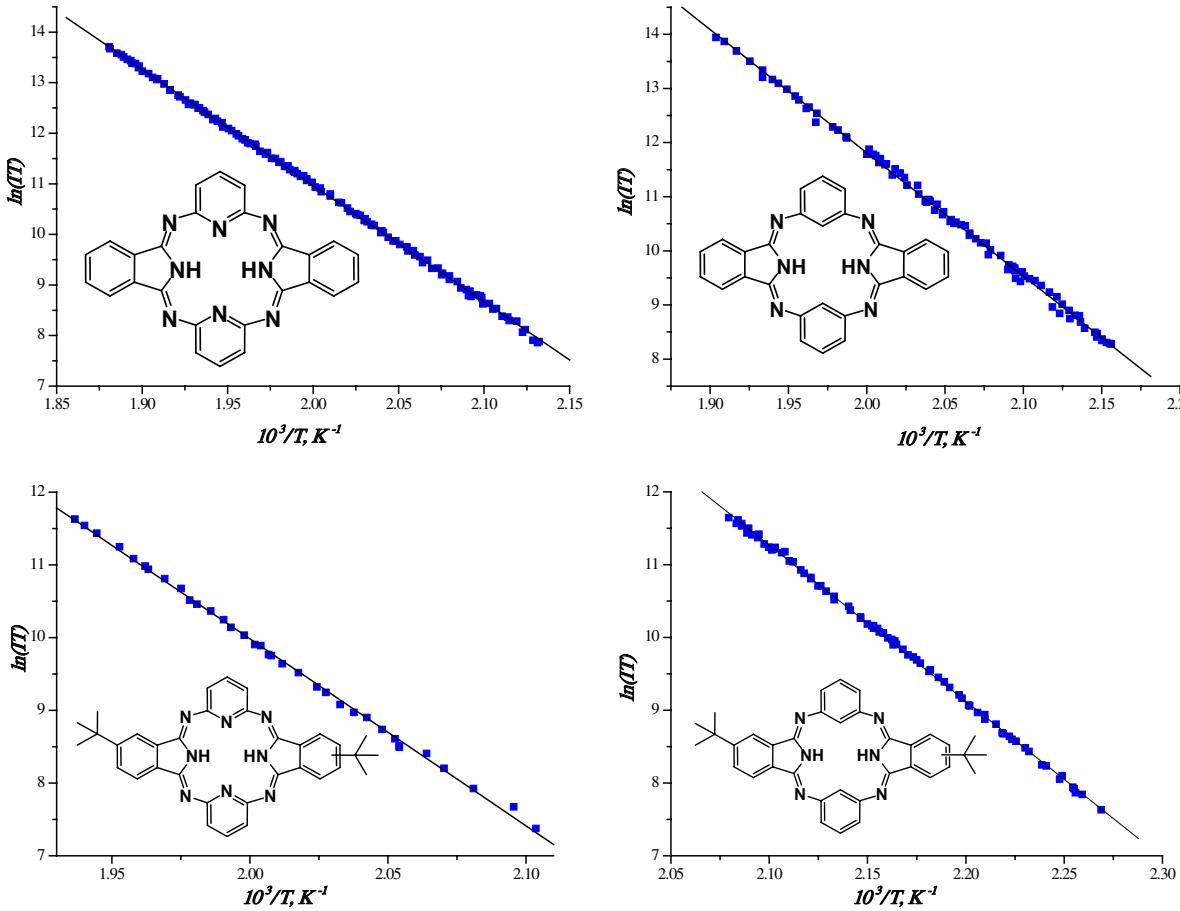



**Fig. 2.** Dependence of the molecular ion intensity logarithm of **5–8** on temperature

**Table 2.** Values of sublimation enthalpies for investigated compounds **5–8**

| Compound | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| $\Delta H°_s$, kJ/mol | 191 (1)* | 189 (3) | 214 (5) | 178 (4) |

* Parenthesized values are estimated errors calculated as $3\sigma_{LS}$.

One can see that hysteresis items are practically absent at temperature increase and decrease. This allows for consideration that the points in the plots correspond to the equilibrium states. The enthalpy of sublimation values $\Delta H_s$ for compounds **5–8** were calculated by linear regression using the Clausius–Clayperon equation and collected in Table 2.

Although the experimental data were not recorded in a broad temperature range, it is considered that the enthalpy of sublimation does not depend on the temperature range under study ($\Delta C_p = 0$).

## CONCLUSION

A new approach consisting of initialization of 2,6-diaminopyridine or 1,3-phenylenediamine with phthalonitrile or 4-*tert*-butylphthalonitrile reactions by microwave irradiation was applied to the synthesis of hemiporphyrazines (**5–8**). It was established that the reactions ran under solvent-free protocol with essential reduction in synthesis duration from 8–12 h to 20 min. Based on mass spectrometric investigations, it was established that hemiporphyrazines **5–8** form a stable stream of particles and their enthalpies of sublimation were estimated using the Clausius–Clayperon equation.

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