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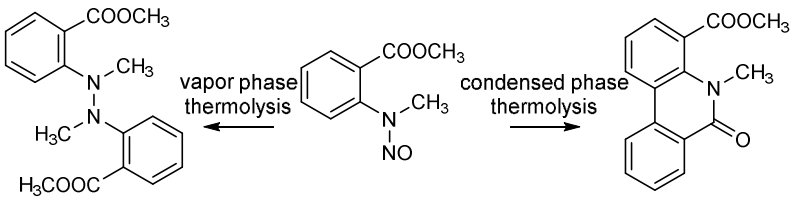

Methyl *N*-methyl-*N*-nitrosoanthranilate thermolysis in the vapor and condensed phases gave different coupling products, dimethyl 2,2'-(1,2-dimethylhydrazine-1,2-diyl)dibenzoate and methyl 5-methyl-6-oxo-(5*H*)-phenanthridine-4-carboxylate, respectively.

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Structural elucidation of thermolysis products of methyl *N*-methyl-*N*-nitrosoanthranilate

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Abstract

Although it is common knowledge that *N*-nitroso compounds are thermally (and otherwise chemically) labile, little or nothing is known of the specific reactions that occur during a thermal treatment of a compound possessing this functionality. Methyl *N*-methyl-*N*-nitrosoanthranilate was found to undergo a complete thermal degradation under gas chromatographic (GC-MS) conditions yielding a major unidentified coupling product and methyl *N*-methylanthranilate. In an attempt to elucidate the structure of the formed degradation product, a preparative scale thermolysis in an evacuated vessel at 220 °C of the nitroso compound was carried out. A chromatographic separation of the thermolysate, followed by GC-MS and NMR (and other spectral techniques) analyses enabled the identification of in total 46 different products. Among them a novel coupling product, methyl 5-methyl-6-oxo-(5*H*)-phenanthridine-4-carboxylate, was identified and fully spectrally characterized. Interestingly, the initially detected coupling product that formed under GC conditions, tentatively identified as dimethyl 2,2'-(1,2-dimethylhydrazine-1,2-diyl)dibenzoate, was not detected in the thermolysate. A careful consideration of the structures of the identified thermolysate constituents led us to a proposition of major thermolysis pathways of methyl *N*-methyl-*N*-nitrosoanthranilate both in condensed and vapor phases. Generally, the identified products could be classified as those arising from fission of the N-NO bond or rather unexpectedly, the Ar-NNO bond, i.e. products related to anthranilic and benzoic acids, respectively. The latter represents a novel chemical transformation up to now unreported

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and unutilized. The structural diversity of the identified products and the noted marked differences between vapor and condensed phases point to possible synthetic utility of thermolysis of carefully designed *N*-nitroso compounds.

Keywords: methyl *N*-methyl-*N*-nitrosoanthranilate, thermal degradation products, gas chromatography-mass spectrometry, 6-(5*H*)-phenanthridinone derivatives, hydrazine derivatives

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Introduction

Although the first report on *N*-nitroso compounds dates back to 1863,[1] there was little interest in the chemistry of this class of compounds for almost a century. As is frequently the case, their biological properties (especially the knowledge that they are carcinogenic) led also to an increased interest in other aspects of these compounds, including their synthesis, mechanisms of formation, chemical and physical properties.[2-7] Only a few *N*-nitroso compounds occur naturally,[7] while most of them can be readily synthesized by nitrosation of secondary amines.[8] They can be formed in the environment, food, tobacco smoke or *in vivo* (e.g. in the stomach) through simultaneous ingestion of nitrosation agents and nitrosable substances.[6, 7, 9]

N-nitroso compounds of low molecular mass (containing three carbon atoms or less) are soluble in water, while most of them are soluble in common organic solvents. Moreover, in the past, they were occasionally used as solvents.[7] Generally, they have favorable partition coefficients into most organic solvents versus water, and there are attempts to link their "liposolubility" to their carcinogenic activity in certain organs.[10] Even though the *N*-nitroso group is not without reactivity, there are few reactions it undergoes. *N*-nitroso compounds are well-known alkylating agents; they can undergo cleavage to produce the parent amines and NO, reduction to give di-substituted hydrazines, and oxidation to yield nitramines.[7, 11, 12] Exposure of nitrosamines' solution to visible light, converts them to amine and nitrite. When it comes to their thermal stability, they are deemed stable at room temperature, while they are being decomposed at temperatures above 200 °C with liberation of NO.[7]

Two secondary amines, isopropyl *N*-methylanthranilate (ternanthranin) and methyl *N*-methylanthranilate (**1**), were subjects of our previous studies in which they showed a number of interesting pharmacological activities.[13-18] Methyl *N*-methylanthranilate is a part of our everyday diet as it naturally occurs in various fruits and plants and is used as a food flavor.[19] Estimated daily oral intake of **1** in Europe is 60 μg/day (1 μg/kg bodyweight/day).[20] Within foodstuff, compound **1** can react with nitrites, which are widely used as food preservatives, to form methyl *N*-methyl-*N*-nitrosoanthranilate (**2**). Besides this, compound **2** can be formed *in vivo*, in the stomach of humans, in the reaction of nitrosation of **1** by nitrites present in the saliva, as well as by the ingestion of nitrite-rich foods.[21] The nitrosation of methyl *N*-methylanthranilate with

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sodium nitrite under conditions similar to those in the human stomach was previously examined by Sakai et al.[22]

Considering a possible formation of methyl *N*-methyl-*N*-nitrosoanthranilate in food and the fact that food frequently undergoes thermal treatment, where thermolysis plays an important role (e.g. baking, frying, grilling, and caramelizing), we decided to investigate the products of methyl *N*-methyl-*N*-nitrosoanthranilate thermolysis. During thermolysis, organic matter undergoes irreversible processes of simultaneous change of chemical composition and physical state, where organic compounds, heated above certain temperature, are being decomposed.[23-26] Depending on the structure of the initial molecule and thermolysis conditions, thermolysate may contain compounds that are the results of decomposition of the initial material and/or compounds formed by the decomposition or recombination of fragments formed from the initial compounds. Having in mind the possible environmental and/or toxicological issues that compounds generated during the process of thermolysis may pose,[23] we decided to carry out a preparative scale thermolysis of compound **2** and to isolate and structurally elucidate (by spectral means and through synthesis) the thermolysate products.

Experimental

Material and methods

Methyl *N*-methylanthranilate (**1**)[13] and methyl *N*-benzoylanthranilate[27] were synthesized according to previously published procedures. All other reagents (methyl anthranilate, benzoyl chloride, sodium nitrite, sodium hydrogen carbonate, hydrochloric acid, anhydrous magnesium sulfate) and solvents (diethyl ether, hexane, chloroform, methanol) were obtained from commercial sources (Sigma-Aldrich, St. Louis, MO, USA; Merck, Darmstadt, Germany; Carl Roth, Karlsruhe, Germany) and used as received, except the solvents were purified by distillation.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance III 400 MHz NMR spectrometer (^{1}H at 400 MHz, ^{13}C at 100 MHz) using $CDCl_3$ as the solvent. Chemical shifts were expressed as δ (ppm) using tetramethylsilane as an internal standard. 2D experiments (^{1}H-^{1}H COSY, NOESY, TOCSY, HSQC and HMBC), as well as DEPT-90 and

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DEPT-135, were run on the same instrument with usual pulse sequences. UV spectra (in acetonitrile) were measured using a UV-1800 Shimadzu spectrophotometer (Tokyo, Japan). Infrared (IR) measurements (attenuated total reflectance) were carried out using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). "Dry flash" chromatography was performed using silica gel 20-45 μm (Carl Roth GmbH + Co.KG, Karlsruhe, Germany). For thin layer chromatography (TLC) silica gel 60 on Al plates (Kieselgel 60 F_{254}, layer thickness 0.2 mm; Merck, Darmstadt, Germany) was used. Spots on TLC were visualized by UV light (254 nm) and by spraying with 10% (w/v) ethanolic solution of phosphomolybdic acid, followed by heating. Microanalysis of carbon, hydrogen and nitrogen were carried out on a Carlo Erba 1106 microanalyzer; their results agreed favorably with the calculated values.

GC and GC-MS analyses

Gas chromatography/mass spectrometry (GC-MS) analyses were repeated three times for each sample using an HP 6890N gas chromatograph coupled with an HP 5975B mass-selective detector (Hewlett-Packard, Palo Alto, CA, USA). The gas chromatograph was equipped with a DB-5MS fused silica capillary column (5% phenylmethylsiloxane, 30 m × 0.25 mm, film thickness 0.25 μm; Agilent Technologies, Palo Alto, CA, USA). The oven temperature was raised linearly from 70 to 315 °C at a heating rate of 5 °C min^{-1} and then held isothermally for 10 min. Helium at a flow rate of 1 mL min^{-1} was used as carrier gas. The injector and interface were maintained at 250 and 320 °C respectively. The samples, 1 μL of the solutions of reaction mixtures or pure compounds in diethyl ether (*ca.* 1 mg in 1 mL of Et_2O), were injected in a pulsed split mode (the flow rate was 1.5 mL min^{-1} for the first 0.5 min and then set to 1 mL min^{-1} for the remainder of the analysis; split ratio 40:1). The mass-selective detector was operated at an ionization energy of 70 eV in the *m/z* 35–500 range with a scanning speed of 0.34 s/scan. Analyses by GC with flame ionization detection (GC-FID) were carried out under the same experimental conditions using the same column as described for GC-MS. The percentage composition was computed from the GC-FID peak areas without the use of correction factors. Qualitative analyses of the reaction mixtures and purified synthesized compounds were based on the comparison of the compounds' linear retention indices relative to the retention times of C_{11}–

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C_{36} *n*-alkanes on the DB-5MS column[28] with those reported in the literature[13, 29, 30] comparison of their mass spectra with those of authentic standards as well as those from Wiley 6, and NIST11; the analysis of fragmentation patterns from mass spectra; the correlation of the calculated boiling points of the tentatively assigned structures with the experimental RI values; and finally, wherever possible, identification was achieved by GC co-injection with an authentic sample.

Synthesis of methyl *N*-methyl-*N*-nitrosoanthranilate

Synthesis of methyl *N*-methyl-*N*-nitrosoanthranilate (**2**) was accomplished following a slightly modified literature method.[22] A solution of 2.77 g (40 mmol) of sodium nitrite in 10 ml of water was added slowly dropwise into a mixture of 3.31 g (20 mmol) of methyl *N*-methylanthranilate (**1**) and 3.32 ml of 37% hydrochloric acid (40 mmol) in 10 ml of water, with stirring at ambient temperature. Afterwards, the mixture was stirred for additional 30 min. The end of the reaction was determined by TLC. The reaction mixture was extracted with diethyl ether; the organic layer was washed with HCl (1%, w/w), water, solution of sodium hydrogen carbonate (2%, w/w) and again with water. The organic layer was then separated, dried over anhydrous magnesium sulfate and the solvent evaporated. The crude product (2.67 g) was purified by an isocratic "dry flash" chromatography (hexane : diethyl ether = 2:1, v/v) to yield a pure sample of methyl *N*-methyl-*N*-nitrosoanthranilate (2.0 g, 52%).

Thermolysis of methyl *N*-methyl-*N*-nitrosoanthranilate

Methyl *N*-methyl-*N*-nitrosoanthranilate (**2**) (0.12 g, 0.62 mmol) was sealed in an evacuated glass tube and heated in an oil bath at 220 °C for 15 minutes. The contents of the vessel were taken up with chloroform. The thermolysate (0.10 g), obtained after the removal of the solvent, was subjected to "dry flash" chromatography on silica gel (20-45 μm) using *n*-hexane-Et_2O (v/v) mixtures of increasing polarity and finally with methanol to furnish 7 fractions (initially pooled based on TLC). The fractions were analyzed by GC-MS and NMR.

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Spectral characterization of the synthesized/detected compounds

Methyl *N*-methyl-*N*-nitrosoanthranilate (**2**) (2.0 g, 52%). Yellowish liquid; UV λ_{max} (CH_3CN)/nm 283sh (log ε 4.59) and 218 (5.20); FTIR (neat) ν_{max}/cm^{-1} 2952.4, 1720.7, 1601.0, 1495.6, 1432.9, 1395.4, 1293.3, 1264.1, 1192.1, 1116.7, 1066.9, 1040.9, 952.6, 762.1, 711.5, 702.7; EIMS *m/z* 194 (M^+, 1.4%), 164 (25.7, M−NO), 133 (14.6, M−OCH_3−NO), 132 (100.0, M−CH_3OH−NO), 105 (19.5, M−$COOCH_3$−NO), 104 (18.5, M−CH_3OH−NO−CO), 77 (38.8, M−$C_3H_5N_2O_3$); Found: C, 55.70; H, 5.22; N, 14.39; O, 24.69%. Calc. for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.19; N, 14.43; O, 24.72%; ^1H and ^{13}C NMR data, see Table 1.

Dimethyl 2,2'-(1,2-dimethylhydrazine-1,2-diyl)dibenzoate (**4**). EIMS *m/z* 328 (M^+, 10.0%), 165 (63.9, M−$C_9H_9NO_2$), 164 (18.2, M−$C_6H_4(NCH_3)COOCH_3$), 163 (22.4, M−$C_9H_{11}NO_2$), 148 (24.4, M−$C_9H_{11}NO_2$−CH_3), 133 (27.6, M−$C_9H_9NO_2$−CH_3OH), 132 (100.0, M−$C_9H_{10}NO_2$−CH_3OH), 118 (10.3, M−$C_{11}H_{16}NO_3$), 105 (69.0, M−$C_9H_9NO_2$−CH_3OH−CO), 104 (58.8, M−$C_9H_9NO_2$−CH_3−H_2O−CO), 91 (12.5, M−$C_{11}H_{13}N_2O_4$), 77 (62.4, M−$C_{12}H_{15}N_2O_4$).

Methyl 5-methyl-6-oxo-(5*H*)-phenanthridine-4-carboxylate (**5**); Yellowish amorphous solid; UV λ_{max} (CH_3CN)/nm 328 (log ε 4.58), 242 (5.19) and 224 (5.18); FTIR (neat) ν_{max}/cm^{-1} 2920.8, 2849.9, 1722.5, 1651.8, 1608.0, 1584.9, 1513.6, 1431.0, 1325.6, 1293.1, 1254.3, 1144.1, 1104.8, 1060.6, 753.3, 722.7, 691.4; Rt 36.941 min, RI (DB-5MS) 2570; EIMS *m/z* 267 (M^+, 100.0%), 252 (25.1, M−CH_3), 236 (78. 7, M−OCH_3), 222 (94.0), 208 (40.6, M−$COOCH_3$), 206 (44.4), 180 (20.7), 179 (31.2), 178 (48.0), 164 (10.2), 152 (37.8), 151 (31.2), 139 (11.8), 117 (10.0), 103 (12.6), 90 (10.6), 89 (11.6), 76 (16.3), 63 (5.9), 51 (2.3); Found: C, 71.86; H, 4.88; N, 5.27; O, 17.99%. Calc. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24; O, 17.96%. ^1H and ^{13}C NMR data, see Table 2. IR, ^1H and ^{13}C NMR spectroscopic data are in accordance with Han et al.[31]

Methyl *N*-benzoylanthranilate (**6**) (1.2 g, 90%). White amorphous solid; UV λ_{max} (CH_3CN)/nm 314 (log ε 4.22), 267 (4.37), 234 (4.64) and 212 (4.72); FTIR (neat) ν_{max}/cm^{-1} 3263.9, 2949.4, 1692.5, 1666.9, 1608.4, 1589.1, 1531.3, 1494.1, 1453.7, 1432.9, 1323.3, 1295.8, 1268.0, 1251.3, 1189.7, 1178.4, 1079.9, 965.8, 896.1, 766.7, 696.4, 664.6; Rt 31.951 min, RI (DB-5MS) 2249; EIMS *m/z* 255 (M^+, 34.0%), 224 (2.2, M−OCH_3), 196 (6.1, M−$COOCH_3$), 105

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(100.0, M−C_6H_4(NH)$COOCH_3$), 90 (3.5), 77 (38.8, M−$C_9H_8NO_3$); Found: C, 70.56; H, 5.12; N, 5.52; O, 18.80%. Calc. for $C_9H_{10}N_2O_3$: C, 70.58; H, 5.13; N, 5.49; O, 18.80%. ^{1}H and ^{13}C NMR data, see Table 3. ^{1}H and ^{13}C NMR spectroscopic data are in accordance with Hinsberger et al.[32]

Methyl *N*-formylanthranilate (**7**). White amorphous solid; UV absorptions: λ_{max} (CH_3CN)/nm 311 (log ε 4.34), 251 (4.77), 244 (4.78) and 221 (5.01) nm; FTIR (neat) ν_{max}/cm^{-1} 3320.1, 2950.0, 1685.4, 1586.1, 1516.2, 1435.0, 1292.0, 1259.5, 1193.3, 1127.3, 1082.4, 963.4, 755.5, 700.7; Rt 18.307 min, RI (DB-5MS) 1568; EIMS *m/z* 179 (M^+, 25.9), 151 (58.9, M−CO), 148 (8.2, M−OCH_3), 146 (10.8), 120 (21.2, M−$COOCH_3$), 119 (100.0, M−OCH_3−CHO), 92 (39.8, M−$COOCH_3$−CO), 90 (10.4), 77 (4.0, M−$C_3H_4NO_3$), 65 (16.2); Found: C, 60.37; H, 5.04; N, 7.84; O, 26.75%. Calc. for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82; O, 26.79%. ^{1}H and ^{13}C NMR data, see Table 3. ^{1}H and ^{13}C NMR spectroscopic data are in accordance with Chen et al.[33] Although, we observed the presence of two rotamers in the NMR spectra, as it was previously published,[33] herein we give only the data for the major rotamer, as the fraction 3 was a complex mixture of several compounds.

Results and discussion

Methyl *N*-methyl-*N*-nitrosoanthranilate (**2**) was prepared by direct nitrosation of methyl *N*-methylanthranilate (**1**, Scheme 1). An NMR analysis of the reaction products verified that there was no methyl *N*-methylanthranilate contamination. However, the ^{1}H NMR contained two sets of analogous signals of unequal intensity (ratio 1 : 12.9). Both sets of signals appeared to correspond to compound **2** based on the chemical shifts and signal multiplicities. An inspection of HSQC and HMBC spectra confirmed the expected C-H connectivity. The most pronounced differences between the chemical shift values belonging to analogous pairs of signals were observed for the NCH_3 and H-3 protons. We believe that the two sets of signals belong to the stereoisomers arising from a hindered rotation about the NN bond (Scheme 1). Table 1 summarizes the NMR data for the two diastereoisomers. We believe that the isomer with the lower chemical shift of NCH_3 protons could be assigned to the (*E*)-isomer based on the antiperiplanar (*trans*) relationship between the lone pair on the nitrogen atom and of the corresponding methyl group (further work in this direction is underway).[34] Although this is a

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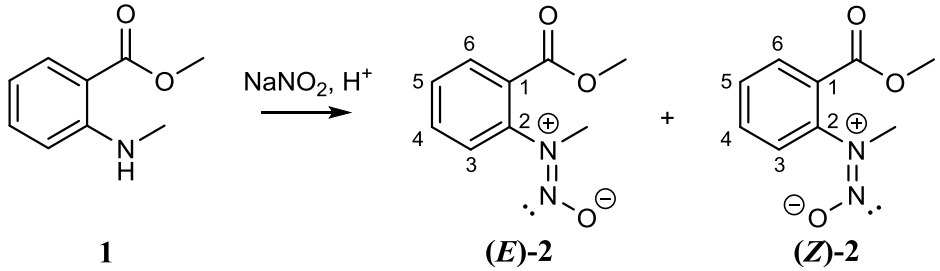
known compound,[22, 35, 36] there was no mention of the existence of stereoisomers and no NMR data provided in the previous work. We did not attempt to separate the two diastereoisomers, and used the obtained mixture in all further experiments.



Scheme 1 Synthesis of methyl *N*-methyl-*N*-nitrosoanthranilate (**2**).

Table 1 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic data ($CDCl_3$; Me_4Si) for compounds **(*E*)-2** and **(*Z*)-2**

Position	(*E*)-Methyl *N*-methyl-*N*-nitrosoanthranilate (**(*E*)-2**)		(*Z*)-Methyl *N*-methyl-*N*-nitrosoanthranilate (**(*Z*)-2**)	
	δ_C, mult.	δ_H (*J* in Hz)	δ_C, mult.	δ_H (*J* in Hz)
1	127.1 C	-	127.0 C	-
2	141.6 C	-	138.9 C	-
3	126.0 CH	7.40, dd (7.9, 1.1)	127.1 CH	7.05, dd (7.8, 1.1)
4	133.0 CH	7.67, td (7.7, 1.6)	133.7 CH	7.64, td (7.7, 1.6)
5	128.9 CH	7.53, td (7.7, 1.1)	129.6 CH	7.49, td (7.7, 1.2)
6	131.4 CH	8.01, dd (7.8, 1.6)	131.3 CH	8.03, dd (8.1, 1.5)
-C̲OOCH$_3$	166.1 C	–	164.9 C	–
-COOC̲H$_3$	52.6 CH$_3$	3.82, s	52.5 CH$_3$	3.82, s
-N(NO)CH$_3$	35.3 CH$_3$	3.41, s CH$_3$	41.0 CH$_3$	4.15, s CH$_3$

A GC-MS analysis (relevant temperatures: injector 250 °C, column 70-315 °C, transfer line 320 °C) of the product revealed an interesting conduct of the compound upon heating. There was no peak corresponding to the expected compound, but instead, the TIC chromatogram (Fig. 1) displayed two peaks eluting at 14.75 min (RI 1419) and 18.66 min (RI 1583) interconnected with an elevated baseline. The first peak (14.75 min), broadened and tailing, belonged to methyl *N*-methylanthranilate (**1**).[13] The mass spectrum of the second, more abundant, compound (18.66

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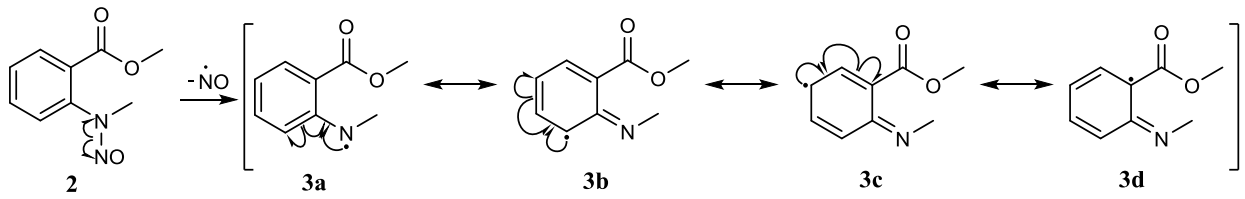
min) was also very similar to the mass spectrum of **1**, but it possessed the highest *m/z* value at 328. An even *m/z* value of $M^{+\bullet}$ pointed to a compound containing an even number of nitrogen atoms. The number of carbon atoms per molecule (18 C) was inferred from the relative intensity of the $[M+1]^+$ ion to the M^+ ion (the ratio of M : [M+1] was found to be 5.0). This and a more precise value of *m/z* of M^+ (328.20) indicated that its molecular formula could be $C_{18}H_{20}N_2O_4$. Inferred from the fragmentation pattern (similar to **1**) and the fact that the molecular formula corresponded to 2 molecules of methyl *N*-methylanthranilate minus 2 H atoms, we could assume that the unknown compound represents the product of an oxidative coupling of two molecules of **1**. Such a reaction can be envisaged as a recombination reaction of two free radicals formed by thermal degradation of compound **2** during the GC experiment where N-NO bond was homolytically cleaved (Scheme 2). As the unpaired electron is expected to be delocalized into the benzene ring, free radicals (**3a-3d**) could be recombined in, in total, six different manners (Fig. 2). Except for **4**, all other structures (**4a-e**) require additional proton transfer steps leading to rearomatization. Sterically and energetically speaking, C-C and C-N coupling of the type in **4a** and **4d** are the most favorable. We believe that the likely structure of this compound would be **4**, and not **4a-e**. Although an N-N bond is significantly weaker than C-N or C-C bonds, the mode of formation (as we have shown below) of this compound limits the complexity (number of steps) of the coupling mechanism. Another possible fate of methyl *N*-methylanthranilate free radicals was an abstraction of a hydrogen atom to give **1** (Rt = 14.754 min).



Scheme 2 Homolytic cleavage of N-NO bond and free radical delocalization.

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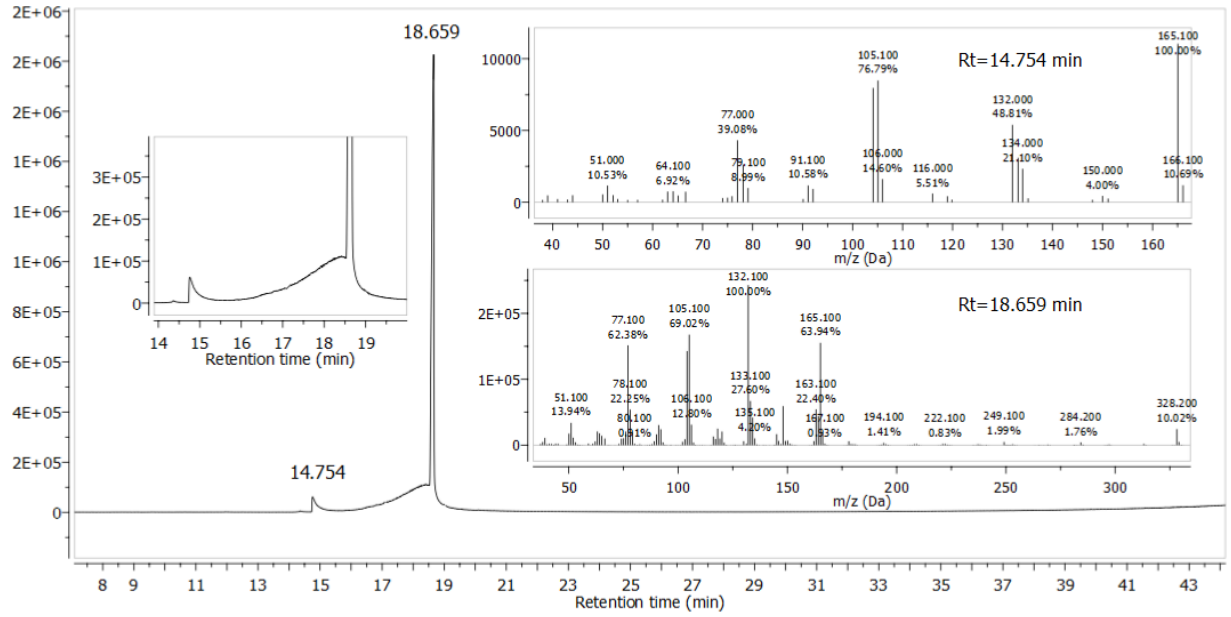

Fig. 1 Gas chromatogram (TIC) of the nitrosation product of **1**.

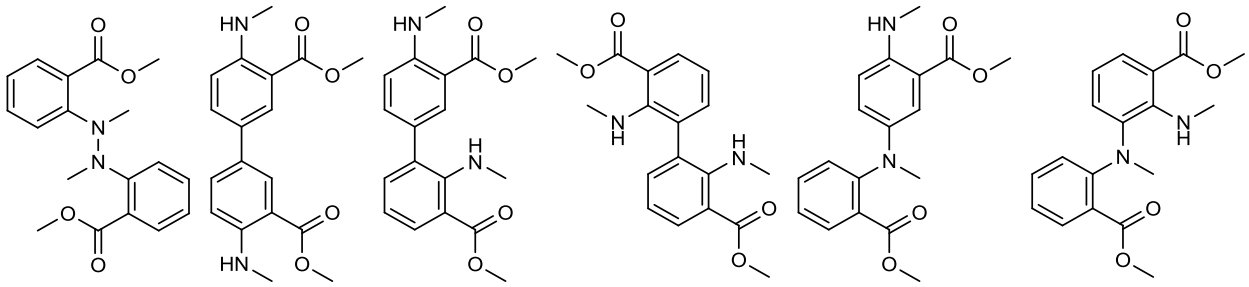

Fig. 2 Possible structures of **4** formed by thermal degradation of **2** during the GC experiment.

The peak shapes (tailing of the methyl *N*-methylanthranilate peak) indicated that one part of methyl *N*-methyl-*N*-nitrosoanthranilate was thermally degraded in the injector (250 °C), while another portion (remaining part) evaporated and was introduced onto the chromatographic column where after (column and/or transfer line) it was subject to further thermal degradation took place. The sharpness of the peak corresponding to compound **4** indicated that it had not form gradually during the GC run but in a short time period, most probably, in the most heated instrument zone-the transfer line (320 °C). Thermal degradation of **2** that happened on the column gave only compound **1** that significantly contributed to the elevated baseline. One can

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assume that the likelihood of hydrogen abstraction from the stationary phase was greater than the probability of radical recombination.

To corroborate the assumption that compound **4** formed in the GC transfer line, and not in the injector or the column, we conducted a series of experiments in which temperature of the GC system was varied (injector, column and transfer line) from 190 to 250 °C. The highest temperature corresponded, naturally, to the transfer line which was always held at least 10 °C above the highest column temperature. Below 220 °C, no degradation of the nitroso compound occurred and a peak of methyl *N*-methyl-*N*-nitrosoanthranilate (**2**) appeared (inferred from the change of the mass scan detected in the same time window). Thus, the coupling product **4** formed in the short period when the nitroso compound reached the transfer line and most probably in the vapor phase (i.e. in the heated helium gas). Such an environment (diluted radicals in an inert gas) allowed only a recombination of two radicals to occur and probably did not provide sufficient time for additional proton transfer reactions (these could not be achieved intramolecularly as sigmatropic rearrangements since they are all forbidden by geometrical constraints/symmetry).

Another fact that is in favor of the formation of the hydrazine derivative, and not biphenyl or diphenylamine derivatives, is that only a single product is observed (no other peaks were detected), under such kinetic control, since almost all other isomers (**4a-e**) are thermodynamically more stable than **4**. Consequently, the likelihood of hydrogen abstraction was much lower and, hence, the formation of **1** was greatly diminished as noted. When making the final decision on the structural assignment of **4**, we took under consideration the general appearance of the observed mass spectrum (strong resemblance to that of the "monomer"), and argued that one should not expect such fragmentation in biphenyl and diphenylamino derivatives (fragmentation that does not involve the cession of bonds leading to monomers should be dominant and give raise to fragments of higher *m/z* than that of the monomer). Thus, we concluded that the structure of **4** was that of dimethyl 2,2'-(1,2-dimethylhydrazine-1,2-diyl)dibenzoate.

To confirm the structure of **4**, we decided to perform a large scale-preparative thermolysis of **2** and to analyze the formed thermolytic products by NMR. Thermolysis of **2** was performed in an evacuated sealed glass vessel heated in an oil bath to 220 °C for 15 minutes. Substantial degradation occurred at that temperature as evidenced by the change in color

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(darkening). The duration of the thermolysis was determined according to a series of experiments with varying time of exposure to heat. The time of 15 min was sufficient for the complete disappearance of **2** (monitored by TLC). After "dry flash" chromatography of the thermolysate, the pooled fractions were analyzed by GC-MS and NMR.

Fraction 4 was pure enough to allow a direct NMR analysis. GC-MS analysis suggested the presence of a major volatile compound eluting at 36.94 min (RI(DB-5MS) 2570). The molecular ion peak at *m/z* 267 was also the base peak. An odd *m/z* value of $M^{+\bullet}$ indicated that the compound in question contained an odd number of nitrogen atoms. This was corroborated by high resolution mass spectrometry that showed that its molecular formula was $C_{16}H_{13}NO_3$. High index of hydrogen deficiency (11 unsaturations) suggested that two molecules of methyl *N*-methyl-*N*-nitrosoanthranilate were combined and that 8 of 11 unsaturations corresponded to 2 aromatic rings. The molecular formula of the investigated compound indicated that it contains 2 C, 7 H, 3 N and 3 O atoms less than those in two molecules of compound **2**.

The presence of 16 C atoms in the molecule was confirmed by 16 peaks observed in ^{13}C NMR among which 5 were peaks of very low intensity. DEPT spectra showed only the existence of CH_3 and CH groups. The ^1H NMR spectra of the compound showed 7 signals in the chemical shifts range of protons attached to an aromatic ring: tree doublets of doublets (dd 7.74, 8.39, 8.54 ppm), two doublets of doublets of doublets (ddd 7.62 and 7.79 ppm), one doublet (d 8.29 ppm) and one triplet (t, 7.33 ppm). This pattern was indicative of 2 aromatic cores, 1,2-disubstitued and 1,2,3-trisubstituted ones. Additionally, there were two signals (singlets at 3.63 and 3.98 ppm) indicating the presence of *N*-methyl and *O*-methyl groups. The structural elucidation and assignation of all proton and carbon-13 NMR signals was made possible only by the use of 2D NMR (^1H-^1H COSY and HMBC spectra) and correlations observed in these spectra gave rise to the assignations given in Table 2**.** The HMBC spectrum showed correlation between the protons at 3.98 ppm and a carbon at 169.3 ppm showing the presence of an ester group. This was also strengthened by the fragmentation patterns visible in the MS spectra, the presence of an ion corresponding to the loss of the OCH_3 group and the loss of $COOCH_3$, and an IR absorption at 1722 cm^{-1}.

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Table 2 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic data ($CDCl_3$; Me_4Si) for the major constituent of fraction 4

Position	δ_C, mult.	δ_H (*J* in Hz)
1	125.2 CH	8.39, dd (8.3, 1.5)
2	121.9 CH	7.33, t (7.8)
3	130.9 CH	7.74, dd (7.5, 1.5)
4	122.4 C	–
4a	137.6 C	–
6	162.8 C	–
6a	125.4 C	–
7	128.8 CH	8.54, dd (8.0, 1.0)
8	128.6 CH	7.62, ddd (8.1, 7.2, 1.0)
9	132.8 CH	7.79, ddd (8.3, 7.2, 1.5)
10	121.8 CH	8.29, d (8.2)
10a	133.1 C	–
10b	121.2 C	–
-$\underline{C}OOCH_3$	169.3 C	–
-$COO\underline{C}H_3$	52.8 CH_3	3.98, s
-NCH_3	36.4 CH_3	3.63, s

The multiplicities and the corresponding coupling constants of protons in ^{1}H NMR and correlations observed in ^{1}H-^{1}H COSY spectrum revealed that the protons at 7.33, 7.74 and 8.39 ppm belong to a trisubstituted aromatic core and the protons at 7.62, 7.79, 8.29 and 8.54 ppm to a disubstituted one. These data generally agreed with two possible structures, presented in Fig. 3. Alongside with the value of chemical shift of the carbonyl which corresponded more to an amide and less to the conjugated ketone, the cross peak between the proton at 3.63 ppm and the carbon at 162.8 ppm in HMBC spectrum confirmed that the *N*-methylamino and carbonyl groups are part of an amide group consistent with structure **5** and are not as distant as in structure **5a**. Structure **5** was additionally confirmed by the existence of cross peaks in the HMBC spectrum (see Fig. 4) and in ^{1}H-^{1}H COSY spectrum (H1-H2, H2-H3, H7-H8, H9-H10). Very recently, during the preparation of this manuscript, the synthesis of **5**, alongside with the spectral data

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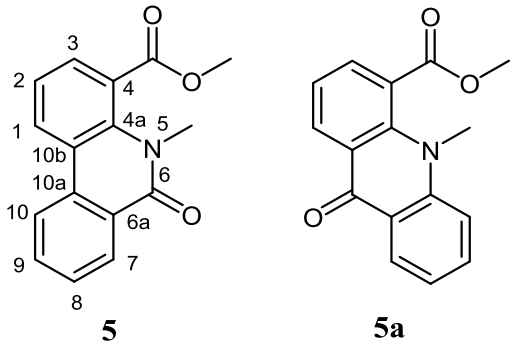
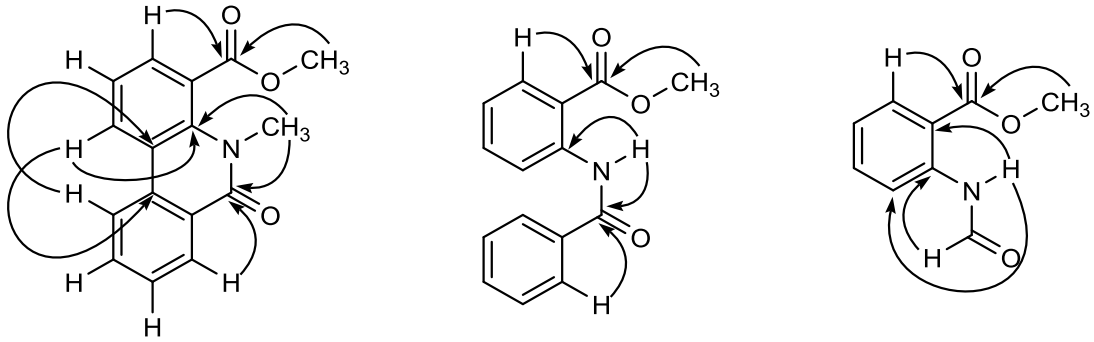
(though without ^{1}H and ^{13}C NMR assignment), has been published.[31] The NMR and IR data published herein agreed favorably with this study.[31]



5 **5a**

Fig. 3 Possible structures of the major constituent of fraction 4.



5 **6** **7**

Fig. 4 Selected HMBC interactions of compounds **5**, **6** and **7**.

A compound eluting at 31.95 min (RI (DB-5MS) 2249), showing the highest *m/z* value at 255 in its mass spectrum, was detected in low amount during the GC-MS analysis of fractions 1, 2 and 3. An odd *m/z* value of $M^{+\bullet}$ (255) pointed to an odd number of nitrogen atoms in the investigated compound and corresponded to the molecular formula $C_{15}H_{13}NO_3$. The comparison of its mass spectra with those from MS libraries suggested that it contained an anthranilate moiety and that it could be an amide of benzoic acid. Having this in mind we assumed that the compound in question was methyl *N*-benzoylanthranilate (**6**) (Fig. 5). To confirm this tentative identification we synthesized the mentioned compound starting from benzoyl chloride and methyl anthranilate in the presence of Et_3N following the procedure of Schneider et al.[27] and the structure of the synthetized compound was confirmed by 1D and 2D NMR (Fig. 4 shows important HMBC interactions used to assign the spectra, while Table 3 summarizes the assigned

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data). NMR data were in accordance with the literature.[32] GC co-injection confirmed that compound **6** was indeed the constituent of fractions 1-3.

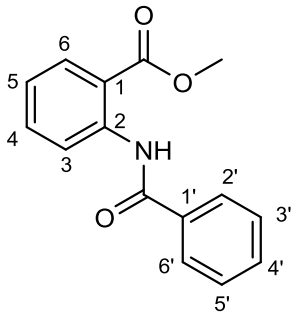

Fig. 5 Structure of compound **6**.

Table 3 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic data ($CDCl_3$; Me_4Si) for compound **6** and **7**

Position	Methyl *N*-benzoylanthranilate (**6**)		Methyl *N*-formylanthranilate (**7**)[a]	
	δ_C, mult.	δ_H (*J* in Hz)	δ_C, mult.	δ_H (*J* in Hz)
1	115.3 C	-	115.2 C	-
2	141.9 C	-	140.8 C	-
3	131.0 CH	8.09, dd (8.1, 1.6)	121.2 CH	8.72 dd (8.6, 1.0)
4	122.6 CH	7.12, ddd (8.1, 7.2, 0.9)	134.8 CH	7.57, ddd (8.6, 7.2, 1.6)
5	134.8 CH	7.61, ddd (8.5, 7.2, 1.6)	123.2 CH	7.11, ddd (8.4, 7.2, 1.0)
6	120.5 CH	8.94, dd (8.5, 0.9)	130.9 CH	8.05, dd (8.4, 1.6)
1’	134.9 C	–	-	-
2’, 6’	127.4 CH	8.06, dd (8.1, 1.6)	-	-
3’, 5’	128.8 CH	7.55, ddd (8.1, 7.6, 0.6)	-	-
4’	132.0 CH	7.53, br d (7.6)	-	-
-COOCH$_3$	169.1 C	–	168.6 C	–
-COOCH$_3$	52.5 CH$_3$	3.13, s	52.5 CH$_3$	3.94, s
-NHCO	165.7 NHCO	12.04, br s	159.6 NHCO	8.52, s NHCHO
				7.55, s NHCHO

[a] The presence of two rotamers was observed in the NMR spectra, as previously reported.[33] However, herein we give only the data for the major rotamer, as the fraction 3 was a complex mixture of several compounds.

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Fraction 3 was a mixture of around twenty compounds among which methyl *N*-formylanthranilate (**7**) (Fig. 6) was the major one (around 50%) (fragmentation patterns visible in the MS spectra (ions corresponding to the loss of the OCH_3 group and the loss of $COOCH_3$ confirmed the presence of an ester group and an ion corresponding to the loss of CO confirmed the presence of an *N*-formyl group)). NMR analysis of fraction 3 (without further purification) corroborated the identity of **7**. ^{1}H NMR contained signals, two dd (8.05 and 8.72 ppm) and two ddd (7.11 and 7.57 ppm), characteristic for an *ortho*-disubstituted aromatic core. All proton and carbon NMR signals were assigned based on 2D NMR (^{1}H-^{1}H COSY and HMBC spectra). For example, the chemical shifts of C1 and C2 were inferred from the HMBC spectrum as these peaks were not observed (low intensity) in ^{13}C NMR. The exchangeable proton attached to the nitrogen atom of -NHCHO was located by two HMBC cross-peaks originating from the coupling of the proton in question with C1 and C3 carbons. Although the presence of two rotamers was observed in our NMR spectra of **7**, as previously reported,[33] herein we report only ^{1}H and ^{13}C NMR data for the major rotamer (Table 3) unambiguously identified in the complex mixture. Important HMBC interactions are presented on Fig. 4.

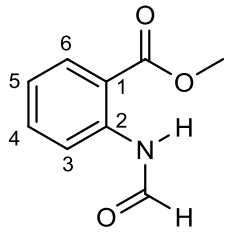

Fig. 6 Structure of compound **7**.

Analysis (GC and GC-MS) of the seven pooled fractions further enabled the identification of 46 different components, representing 25.2-94.7% of the peak areas detect for the individual fractions. The identified constituents, their relative share in the fractions, molar masses, Rt and RI values and methods of identification are listed in Table 4. Three arguments were taken into account when a final decision was made to ascribe a certain structure to a peak. The molecular mass and the MS fragmentation patterns were used to propose a tentative chemically sound structure that might be expected from the thermolytic process. The meaningfulness of the proposed structures was further tested by a correlation analysis of the

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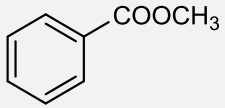
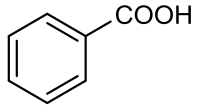
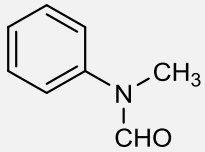
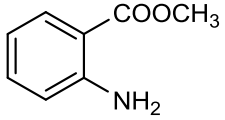
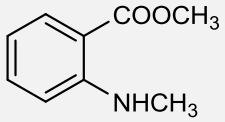
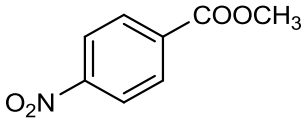
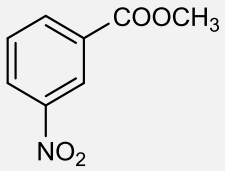
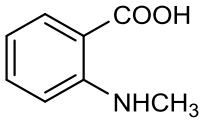
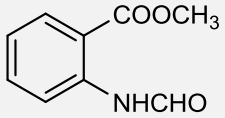
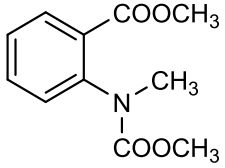
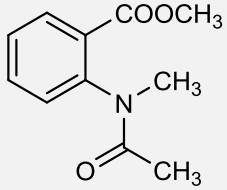
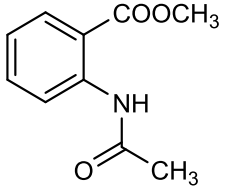
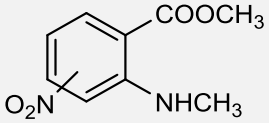
predicted boiling points (*Bp*) for these structures (ChemBio3D Ultra 13.0) and their experimental retention indices (*RI*)[37] since literature indices for the majority of the detected compounds could not be found in the literature. All compounds that showed a significant deviation (30 K or more) of the estimated *Bp* by the correlation equation from the calculated *Bp* were omitted from the list of correctly identified compounds, and this was redone several times until a good correlation was attained. The final correlation equation of predicted *Bp* vs *RI* are given below:

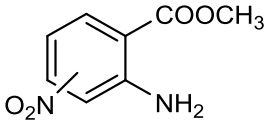
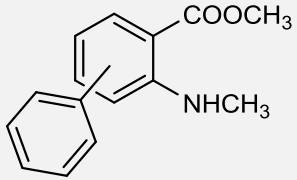
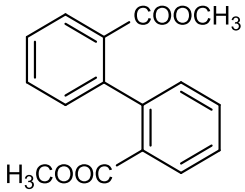
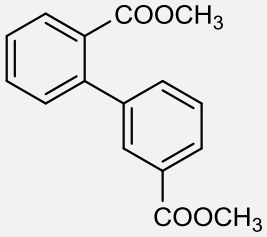
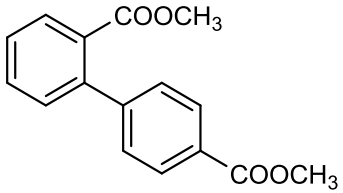
$Bp = 351.73604 + 0.14209RI$, R = 0.95742.

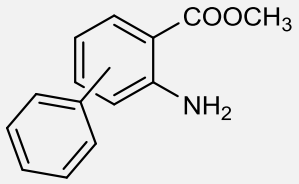
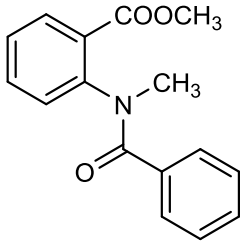
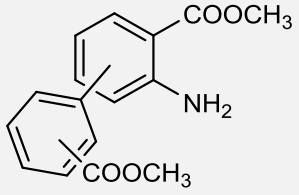
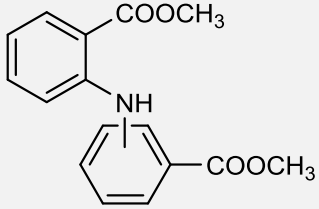
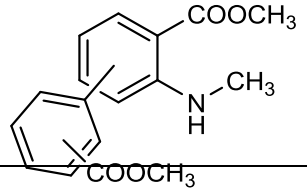
where *Bp* represents the predicted boiling point of a compound, *RI* represents its experimental retention index, while R is the correlation coefficient.

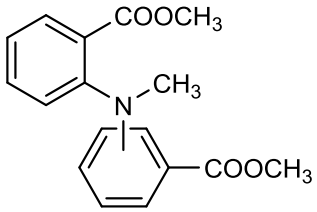
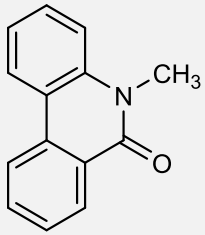
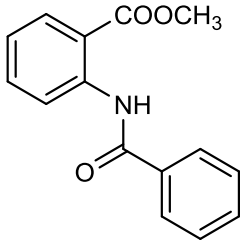
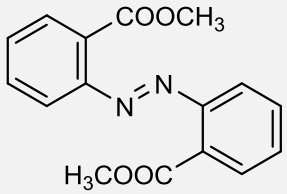
Table 4 The preparative-scale thermolysis products of compound **2**

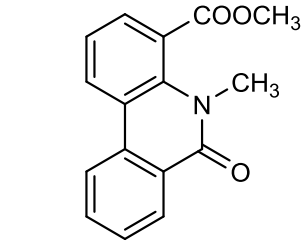
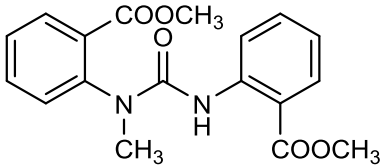
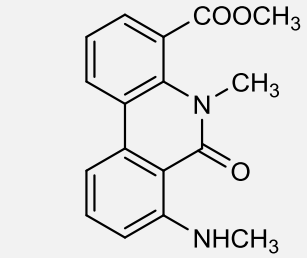
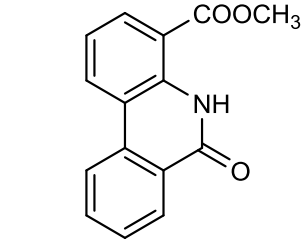
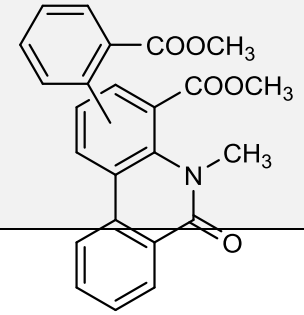
N^{o}	Compound structure[a]		M [g/mol]	Rt [min]	RI	IdenMeth[b]	Fr1 [%]	Fr2 [%]	Fr3 [%]	Fr4 [%]	Fr5 [%]	Fr6 [%]	Fr7 [%]
1.		(**8**)	136	6.989	1103	RI, MS, CoI	0.3	tr	-	-	-	-	-
2.		(**9**)	122	8.979	1181	RI, MS, CoI	-	0.1	0.3	-	-	-	-
3.		(**10**)	135	11.545	1285	RI[a], MS	-	tr	0.1	-	-	-	-
4.		(**11**)	151	13.181	1353	RI, MS, CoI	4.0	10.7	0.2	-	tr	4.0	1.7
5.		(**1**)	165	14.754	1419	RI, MS, CoI	82.7	15.8	5.4	-	0.9	1.3	0.3
6.		(**12**)	181	15.697	1458	RI, MS	-	18.8	2.0	-	-	-	-

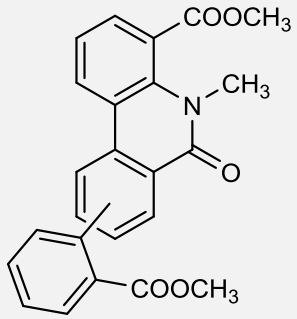
7.		(**13**)	181	16.385	1486	RI, MS	-	0.2	-	-	-	-	-
8.		(**14**)	151	16.808	1503	RI[a], MS, CoI	-	0.8	0.2	-	-	-	-
9.		(**7**)	179	18.307	1568	RI[a], MS, NMR	-	18.3	48.7	-	tr	3.3	-
10.		(**15**)	223	18.988	1597	RI[a], MS	-	-	-	-	1.1	-	-
11.		(**16**)	207	19.152	1605	RI[a], MS[a]	-	0.1	0.7	-	-	-	-
12.		(**17**)	193	19.241	1609	RI[a], MS	-	0.2	0.2	-	-	-	24.8
13.		(**18**)	210	19.650	1627	RI[a] , MS	-	1.4	1.1	-	-	-	tr

14.		(**19**)	196	21.001	1688	RI[a], MS	-	tr	tr	-	tr	tr	-
15.		(**20**)	241	24.767	1869	RI[a], MS[a]	tr	0.1	-	-	-	-	-
16.		(**21a**)	270	25.842	1923	RI[a], MS	-	2.7	0.3	-	tr	-	-
17.		(**21b**)	270	29.001	2081	RI[a], MS	0.6	3.4	0.1	-	tr	-	tr
18.		(**21c**)	270	29.434	2102	RI[a], MS[a]	0.5	1.8	0.1	-	tr	-	-

19.		(**22**)	227	26.343	1949	RI[a], MS[a]	tr	tr	-	-	-	-	-
20.		(**23**)	269	29.374	2099	RI[a], MS[a]	-	-	-	-	tr	0.5	0.8
21.		(**24**)		29.924	2130	RI[a], MS[a]	-	0.1	tr	1.6	tr	tr	tr
22.				32.862	2304	RI[a], MS[a]	1.1	0.6	0.2	-	-	-	tr
23.				32.964	2311	RI[a], MS[a]	tr	0.1	-	-	tr	-	-
24.	and/or		285	33.641	2353	RI[a], MS[a]	-	0.3	0.7	1.3	-	-	tr
25.		(**25**)		33.694	2357	RI[a], MS[a]	-	tr	-	-	2.1	tr	tr
26.				34.195	2389	RI[a], MS[a]	0.2	0.1	0.1	-	-	0.4	tr
27.				35.985	2505	RI[a], MS[a]	-	tr	tr	-	-	tr	0.2
28.		(**26**)	299	30.577	2167	RI[a], MS[a]	-	0.2	tr	-	tr	-	tr
29.				30.790	2180	RI[a], MS[a]	0.4	3.8	0.2	0.4	-	0.4	-

30.	and/or			31.792	2240	RI[a], MS[a]	-	tr	-	-	-	-	-
31.		(**27**)		32.268	2269	RI[a], MS[a]	0.3	0.7	tr	-	-	-	-
32.				34.085	2382	RI[a], MS[a]	2.1	1.9	0.1	1.7	tr	tr	tr
33.				34.591	2414	RI[a], MS[a]	1.2	2.3	tr	1.3	tr	tr	tr
34.		(**28**)	209	31.016	2194	RI[a], MS[a]	-	-	0.2	-	-	-	-
35.		(**6**)	255	31.951	2249	RI[a], MS[a], CoI, NMR	0.8	0.4	tr	-	-	-	-
36.		(**29**)	298	33.090	2319	RI[a], MS[a]	0.5	0.5	0.5	-	tr	tr	tr

37.		(**5**)	267	36.941	2570	RI[a], MS[a], NMR	-	-	4.8	80.8	51.7	1.5	tr
38.		(**30**)	342	37.020	2576	RI[a], MS[a]	-	tr	-	tr	3.5	-	-
39.		(**31**)	296	37.060	2578	RI[a], MS[a]	-	-	-	-	-	-	0.7
40.		(**32**)	253	37.291	2594	RI[a], MS[a]	-	-	tr	5.5	6.5	-	-
41.		(**33**)	401	46.742	3320	RI[a], MS[a]	-	-	-	-	-	2.7	1.1
42.				46.866	3331	RI[a], MS[a]	-	-	-	-	-	1.7	0.4

43.		(**34**)	48.008	3430	RI[a], MS[a]	-	-	-	-	-	2.9	1.7
44.			49.288	3544	RI[a], MS[a]	-	tr	-	-	-	2.4	0.6
45.			50.333	-	RI[a], MS[a]	-	-	-	-	-	2.6	0.6
46.			51.392	-	RI[a], MS[a]	-	-	-	-	-	1.5	1.3
	Total identified					94.7	85.4	66.2	92.6	65.8	25.2	34.2

[a] Compounds listed in order of elution on DB-5MS column (Rt: retention time (in min) and RI: experimentally determined retention indices on the mentioned column by co-injection of a homologous series of *n*-alkanes C_{11}–C_{36}).

[b] RI, constituent identified by retention index matching; RI[a], identification corroborated by the correlation of the calculated boiling point of the tentatively assigned structure with the experimental RI value; MS, constituent identified by mass spectra comparison; MS[a], identification based on mass spectral fragmentation pattern; CoI, constituent identity confirmed by GC co-injection of authentic sample; NMR, structure of an isolated pure constituent confirmed by ^{1}H and ^{13}C NMR spectral analysis.

tr, trace amount (less than 0.05%); -, compound not detected in this particular chromatographic fraction.

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Although compound **4** was not detected among the products of methyl *N*-methyl-*N*-nitrosoanthranilate thermolysis in condensed phase, listed in Table 4, we correlated its predicted boiling point (*Bp*) and experimental retention index (RI). Based on the above equation, the *RI* value of **4** should be around 2500 which is almost 1000 RI units higher than the one we found (RI 1583) in the early experiments. This discrepancy supported the fact that a significant portion of **2** passed through the GC column unaltered and was completely decomposed in the much warmer transfer line where the recombination of the methyl *N*-methylanthranilate radicals took place (i.e. the part of the nitroso compound that did not decompose in the injector and column, completely transformed to the coupling product **4** in the transfer line and this explains the fast "elution" of **4** from the GC column since it formed only at the very end of the same).

A careful consideration of the structures of the identified thermolysate constituents led us to a proposition of the major thermolysis pathways of methyl *N*-methyl-*N*-nitrosoanthranilate. Since none of the identified products contained a nitroso group, compound **2** initially must have undergone a cleavage of either N-NO or C_{Ar}-NNO bonds. N-NO bond appears to be a good candidate for homolytic cleavage as one would expect from the stability of NO and a delocalized methyl *N*-methylanthranilate radical (Scheme 2). A high number of products appears to have formed in the reaction of the radical (**3a-d**) that was obtained as the result of the mentioned homolytic cleavage of N-NO bond (**1**, **11**, **14**, **31**, and in part **5**, **6**, **20**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **32**, **33, 34**).

Furthermore, we identified quite a few simple derivatives of benzoic acid, i.e. products lacking the *ortho*-$NHCH_3$ group (**8**, **9**, **21a-c**, in part **20**, **22**, **24**, **25**, **26**, **27**, **33**, **34**). These products could have formed either from a hypothetical methyl benzoate radical (**35**) or in the hypothetical reaction of methyl *N*-methylanthranilate radical (**3**) with methyl benzoate (**8**). The origin of **8** and **35** is not clear to us, although there is a possibility that during the thermolysis, besides the N-NO, C_{Ar}-NNO homolytic cleavage could have occurred, as well (Scheme 3). Other more elaborate mechanisms of methyl benzoate-related species formation could be envisaged (Scheme 4). However, at this moment, we cannot dismiss any of the possibilities or even rule out their concurrent existence. Both N-NO and C_{Ar}-NNO cleavages seem to be likely as methyl *N*-methylantranilate (**1**) and methyl benzoate (**8**) would arise from hydrogen abstraction by these radicals (**3a-d** and **35**, respectively). Beside hydrogen abstraction, these radicals could recombine in several ways or could react with compounds **1** and **8** to give numerous products that could

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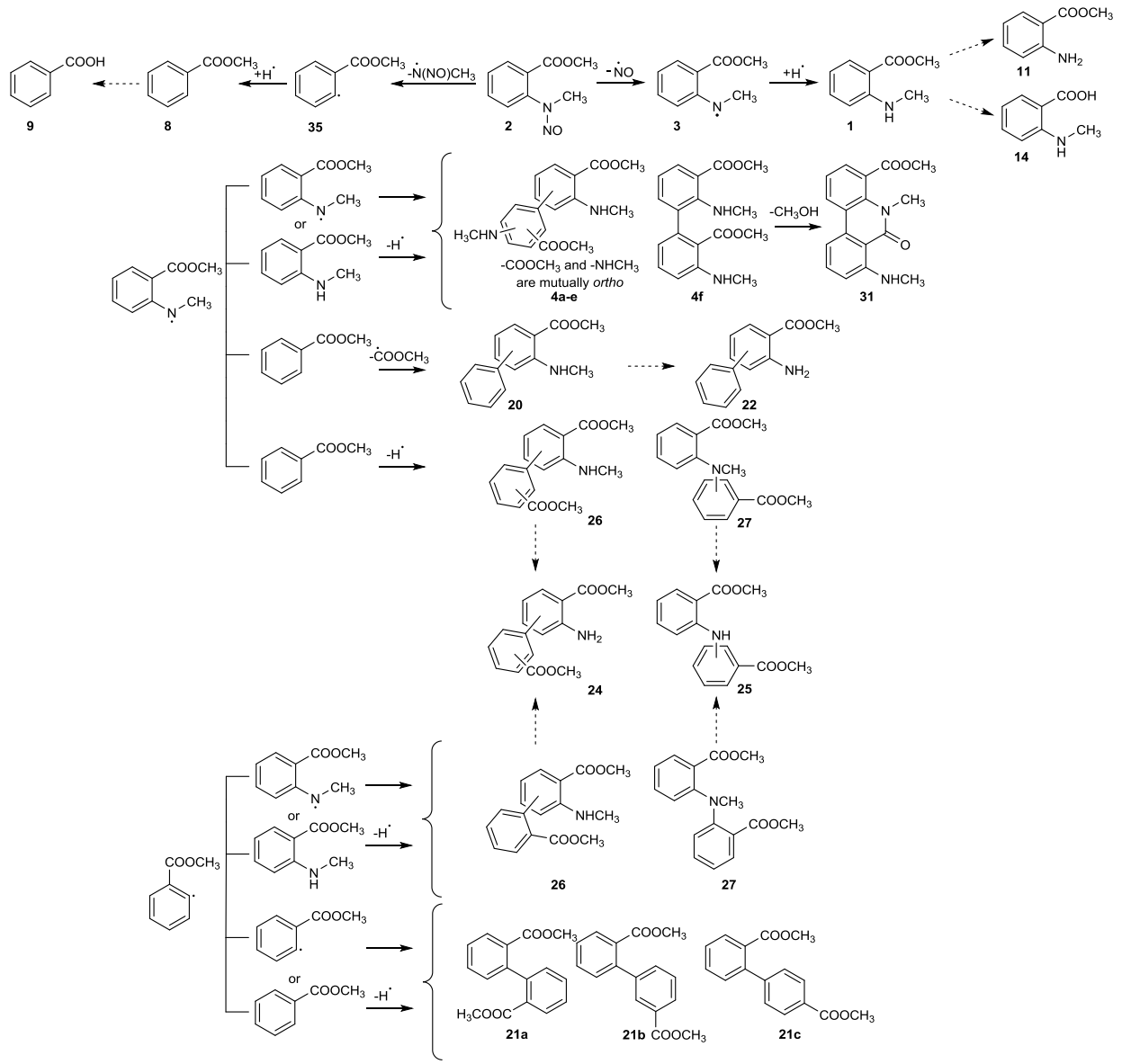
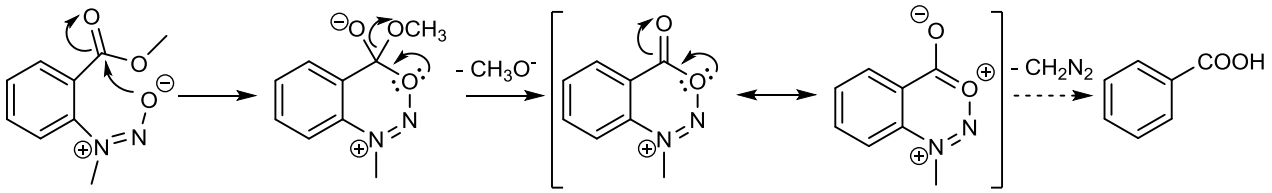
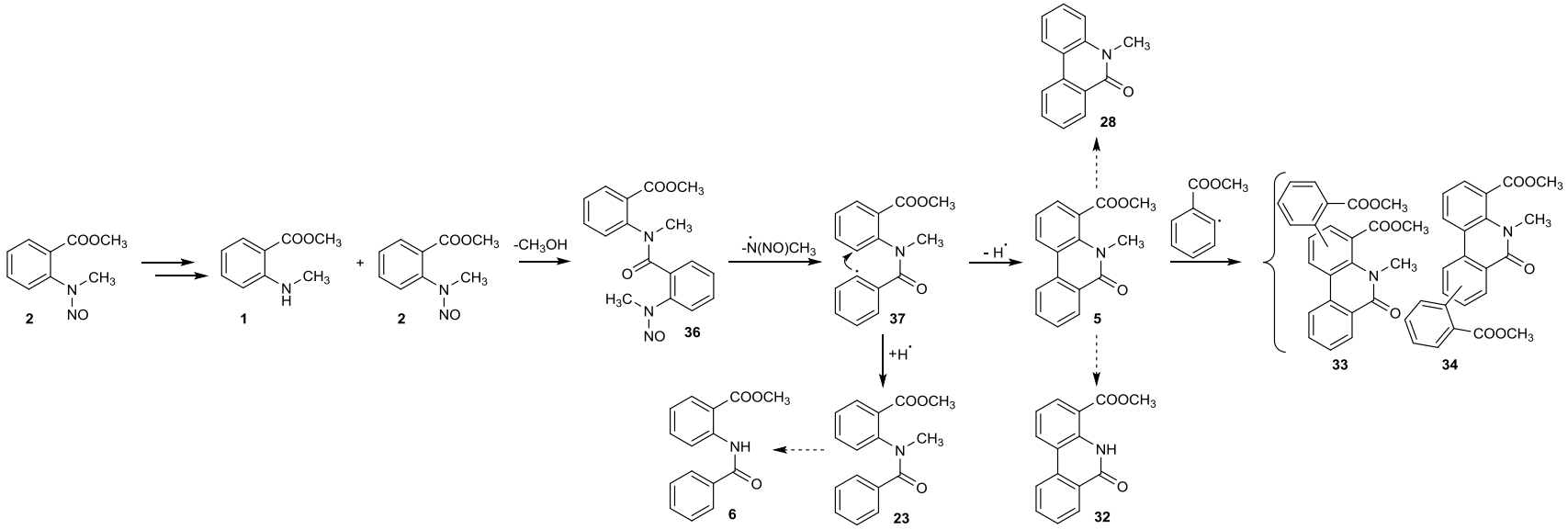
undergo further modifications (e.g. *O*- or *N*-demethylation and decarboxylation) (Scheme 3 and 5).



Scheme 3 Possible pathways of thermolysate products formation.



Scheme 4 Possible mechanism of methyl benzoate (**8**) formation.



Scheme 5 Additional pathways of thermolysate products formation in the condensed phase.

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Two methyl *N*-methylanthranilate radicals could recombine in several different ways as mentioned above (structures **4** and **4a-e**). Neither of these products was detected as the product of methyl *N*-methyl-*N*-nitrosoanthranilate thermolysis in condensed phase. However, there was a possibility that radical **3b** reacted with **1** to give **4f**, another regioisomer of structure **4**. Although we did not find **4f** during the analysis of the seven pooled fractions, we assume that it did form during the thermolysis, but due to a suitable orientation of $-NHCH_3$ and $-COOCH_3$, it subsequently underwent intramolecular aminolysis which led to the formation of the six-member lactam **31** detected in fraction 7.

Another fate of methyl *N*-methylanthranilate free radical is to react with methyl benzoate radical, or methyl benzoate to give **26** and/or **27**. In the case of the recombination of methyl *N*-methylanthranilate and methyl benzoate radicals, the number of possible regioisomeric products is lower than in the case of methyl *N*-methylanthranilate radical reacting with methyl benzoate. The unpaired electron of methyl benzoate radical is not delocalized and the newly formed C_{Ar}-C_{Ar} bond has to be *ortho*- to the $-COOCH_3$ group of methyl benzoate. Methyl *N*-methylanthranilate radical and methyl benzoate could react in such a way, ipso attack, to allow a consequent decarboxylation of methyl benzoate leading to compound **20**. Compounds **20**, **26** and **27** were found to further undergo *N*-demethylation to yield **22**, **24**, and **25**, respectively.

One more possible reaction pathway, occurring during the thermolysis in the condensed phase, is that methyl *N*-methyl-*N*-nitrosoanthranilate undergoes aminolysis with methyl *N*-methylanthranilate to give **36** which undergoes a homolytic cleavage of the C_{Ar}-NNO bond (Scheme 5). The newly formed radical (**37**) could abstract $H^{\bullet}$ to give **23** or to undergo intramolecular cyclisation to form **5**. Furthermore, compound **5** could be *N*-demethylated to give **32**, decarboxylated to give **28** or could react with methyl benzoate radical to give compounds **33** and/or **34**. Another possible way of compound **23** formation is the aminolysis of methyl benzoate by methyl *N*-methylanthranilate. Moreover, beside the abovementioned reactions, where the aromatic core of at least one of the reactants was involved, another group of compounds detected in the thermolysate indicated that during thermolysis acylation also took place (**7**, **6**, **10**, **15**, **16**, **17**, **23**, **30**). For example, compound **16** was formed by acetylation of **1**. Two mechanisms of formation of **6** and **17** were possible: demethylation of **23** and **16**, respectively; or **6** could have formed as the result of aminolysis of methyl anthranilate (**11**) and methyl benzoate (**8**), while **17**

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is the acetylation product of **11**. Also, two formylation products (**7** and **10**) were identified. The origin of acetic and formic acids remains unclear.

A recombination of two methyl benzoate radicals could give only **21a**, whereas the reaction of methyl benzoate radical and methyl benzoate could yield **21a**, **21b** and **21c**. The thermolysate contained four nitro compounds, two of them were nitro-derivatives of methyl benzoate (**12** and **13**), while **18** and **19** resulted from a hypothetical nitration of the methyl esters of anthranilic and *N*-methylanthranilic acids, respectively. The azo compound (**29**) probably formed by coupling of two molecules of methyl *N*-methyl-*N*-nitrosoanthranilate and a subsequent oxidation.

Conclusion

To summarize, we identified two products of methyl *N*-methyl-*N*-nitrosoanthranilate thermolysis in the vapor phase, and 46 different products formed by its thermolysis in the condensed phase. Thermolysis of **2** in the vapor phase gave a coupling product, tentatively identified as dimethyl 2,2'-(1,2-dimethylhydrazine-1,2-diyl)dibenzoate, as the major one, and methyl *N*-methylanthranilate. Among 46 products of thermolysis of **2** in the condensed phase, methyl 5-methyl-6-oxo-(5*H*)-phenanthridine-4-carboxylate, a coupling product completely different from the one obtained by thermolysis in vapor phase, was identified. A careful consideration of the structures of the identified thermolysate constituents led us to a proposition of the major thermolysis pathways of methyl *N*-methyl-*N*-nitrosoanthranilate both in condensed and vapor phases.

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