## **Brief Communications**

## Reductive chlorination of bis(4-tert-butylphenyl)amine-N-oxyl nitroxyl radical

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Unlike cyclic aliphatic nitroxyls, whose oxidation with halogens gives oxoammonium salts, bis(4-tert-butylphenyl)amine-N-oxyl (1) treated with chlorine undergoes reductive chlorination to the corresponding di- and trichlorodiphenylamines. Chlorine partially dealkylates the compounds obtained. Plausible mechanisms for these reactions were suggested.

Key words: nitroxyl radicals, oxoammonium salts, chlorination.

Oxoammonium salts are widely used in organic synthesis as stoichiometric oxidants and catalysts of oxidation of alcohols to carbonyl compounds.<sup>1-5</sup> A principal method for the synthesis of these salts is the oxidation of nitroxyl radicals with halogens and variable valence metal halides.5

In order to synthesize sterically hindered oxoammonium salts, we studied the oxidation of bis(4-tert-butylphenyl)amine-N-oxyl (1) with chlorine. However, instead of the expected oxoammonium salt 2 the reaction of this amine-N-oxyl with chlorine was found to lead to a mixture of chloroamines 3-9, which were isolated in the individual state.

The structure and composition of chloroamines 3–9 were confirmed by elemental analysis and NMR, UV, IR, and mass spectra (see Experimental). Positions of chlorine atoms in chloroamines 3-8 were established using the <sup>1</sup>H<sup>-1</sup>H NOE NMR spectra based on the signal enhancement effects of tert-butyl groups and benzene protons. Dichloroamine 3 was also obtained by an alternative synthesis from bis(4-tert-butylphenyl)amine (10), whereas tetrachlorodiphenylamine 9 has been known<sup>6</sup> since 1875. Besides chloroamines 3-9, the reaction gave tert-butyl chloride (26 mol.%), HCl (4 mol.%), water, and some unidentified products detected by chromatography. The major chlorination products of amine-N-oxyl 1 are chloroamines 3-5, which were formed in 35, 34, and 23 mol.% yield, respectively.

Reductive chlorination of amine-N-oxyl 1 to trichloroamine 4, apparently, results from the sequential reduction of the nitroxyl group of amine-N-oxyl 1 with the benzene hydrogen atoms, which are replaced by the chlorine atoms according to Scheme 2.

In the first step, chlorine adds to the benzene ring of amine-N-oxyl 1 with the formation of nitrone 11, which isomerizes to chlorohydroxylamine 12. As a result, the benzene hydrogen atom is shifted to the nitroxyl group with its one-electron reduction. The addition of the second chlorine atom to the benzene ring of chlorohydroxylamine 12 leads to adduct 13, which elimi-

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nates water to give aminyl radical 14. Hydroxylamine 12 undergoes a one-electron reduction to aminyl 14. The addition of the third chlorine atom to aminyl 14 results in imine 15, which isomerizes to trichloroamine 4. The sum of these sequential reactions is the stoichiometric equation (1).

$$\mathbf{1} + 1.5 \operatorname{Cl}_2 \longrightarrow \mathbf{4} + \operatorname{H}_2 \mathbf{0} \tag{1}$$

Dichloroamine 3 is probably formed in the reaction of the intermediate chlorohydroxylamine 12 with HCl according to Scheme 3.

Chlorohydroxylamine 12 like other N,N-diarylhydroxylamines<sup>7</sup> in the reaction with HCl is converted to salt 16, which through imine 17 isomerizes to the final dichloroamine 3. The sum of the reactions in Scheme 3 and the first reaction in Scheme 2 correspond to the stoichiometric equation (2).

Н

10

Bu

But

$$\mathbf{1} + 0.5 \operatorname{Cl}_2 + \operatorname{HCl} \longrightarrow \mathbf{3} + \operatorname{H}_2 \mathbf{O}$$
 (2)

Hydrogen chloride is apparently formed by the elimination of hydrogen atoms with chlorine from the intermediate compounds 11 and 13. Trichloroamine 5 and tetrachloroamine 9 are formed by the dealkylation of dichloroamine 3 with chlorine according to Scheme 4.



Scheme 2

Scheme 3









Chlorine adds to the *para*-position of benzene rings of dichloroamine 3 with the formation of adduct 18, which is converted to trichloroamine 5 and Bu<sup>t</sup>Cl. Similarly, tetrachloroamine 9 forms from trichloroamine 5, whereas tetrachloroamines 8 and 7 form from trichloroamine 4 in the ratio 1 : 12. The total amount of dealkylated amines 5 and 7-9 (26.5 mol.%) corresponds to the amount of Bu<sup>t</sup>Cl formed (26 mol.%). A small amount of tetrachloroamine 6 is apparently formed by the chlorination of trichloroamine 4 at *ortho*-position of the benzene ring.

Oxoammonium salt 2 is probably formed by the oxidation of amine-N-oxyl 1 with chlorine. However, it is unstable and adds the anion Cl<sup>-</sup> to oxoammonium cation to be converted to chlorohydroxylamine 12 through nitrone 11. The latter is also formed by the reductive chlorination of amine-N-oxyl 1 (see Scheme 2). Therefore, the final decomposition products of salts 2 and the reductive chlorination products of amine-N-oxyl 1 are identical.

In conclusion, amine-N-oxyl 1 is converted to chloroamines 3 and 4 as a result of three-electron reductive chlorination. The reductive chlorination is accompanied by dealkylation of amine-N-oxyl 1 and chloroamines 3 and 4 with chlorine.

## Experimental

Bis(4-*tert*-butylphenyl)amine-*N*-oxyl (1) was obtained according to the procedure published earlier<sup>8</sup> and crystallized from methanol, m.p. 137 °C. Bis(4-*tert*-butylphenyl)amine (10) was

obtained according to the described procedure<sup>9</sup> and crystallized from methanol, m.p. 108 °C. Chromatographic analysis was performed on a Milikhrom chromatograph (2×64-mm column, Separon C18, 5  $\mu$ m), detection at 280 nm, eluent 80% aqueous MeCN. IR reflection spectra were recorded on a Spectrum 100 spectrometer, whereas absorption spectra on a Specord 75IR spectrometer. NMR spectra were recorded on a Bruker AIII spectrometer (500 MHz) in chloroform-d<sub>1</sub>. The NMR signals were assigned based on the 2D <sup>1</sup>H-<sup>13</sup>C HSQC spectra and <sup>1</sup>H-<sup>1</sup>H NOE. UV spectra were recorded on a Specord UV-VIS spectrometer, electron impact mass spectra (70 eV) were obtained on a Finnigan chromato-mass spectrometer. Melting points were determined on a RNMK heating stage.

Chlorination of bis(4-tert-butylphenyl)amine-N-oxyl (1). A solution of chlorine (107 mg, 1.5 mmol) in CCl<sub>4</sub> (2 mL) was added to a solution of amine-N-oxyl 1 (296 mg, 1 mmol) in CCl<sub>4</sub> (3 mL) cooled in an ice bath. After ~10 min, the solvent and the volatile reaction products (H<sub>2</sub>O and Bu<sup>t</sup>Cl) were evaporated in vacuo. The distillate was dried, the amount of ButCl formed (24 mg, 0.26 mmol) was determined based on the band at 1368 cm<sup>-1</sup> ( $\epsilon$  = 74.8 L mol<sup>-1</sup> cm<sup>-1</sup>) in the IR spectrum. The product (410 mg) was obtained after evaporation of the distillate, the HPLC data,  $V_{ret}/\mu L (I_{rel} (\%))$ : 360 (7.9), 385 (8.0), 425 (4.0) 9, 475 (4.0), 520 (3.1) 7, 8, 613 (1.0), 650 (77) 5, 720 (60) 4, 865 (2.1) 6, 970 (100) 3. The quantitative HPLC analysis showed that this product contained dichloroamine 3 (124 mg, 35%), trichloroamine 4 (131 mg, 34%), trichloroamine 5 (76 mg, 23%), tetrachloroamine 6 (8.4 mg, 2%), tetrachloroamines 7 and 8 (7.3 mg, 2%), and tetrachloroamine 9 (4.6 mg, 1.5%). The reaction product was dissolved in heptane (10 mL), followed by addition of silica gel (5  $\text{cm}^3$ ). The silica gel with the absorbed resin was filtered off and washed thrice with heptane. Evaporation of heptane gave a mixture of products (330 mg), which was separated on a chromatographic column (30×153 mm, Separon SGX C18, 20 µm), eluting with 90% aq. MeCN, composition of the eluate was monitored by HPLC. On this column, the compound  $V_{\rm ret}$  was ~550 times higher than on the analytical column. The separation yielded dichloroamine 3 (99 mg), trichloroamine 4 (104 mg), trichloroamine 5 (60 mg), tetrachloroamine 6 (6.5 mg), a mixture of tetrachloroamines 7 and 8 (5.5 mg), and tetrachloroamine 9 (4 mg).

Bis(4-tert-butyl-2-chlorophenyl)amine (3). A. A solution of chlorine (242 mg, 3.4 mmol) in CCl<sub>4</sub> (5 mL) was added over ~5 min to a solution of amine 10 (951 mg, 3.38 mmol) in CCl<sub>4</sub> (3.5 mL) cooled in an ice bath. The reaction mixture was stirred for ~20 min with cooling. A precipitate of amine 10 hydrochloride (585 mg) was filtered off, the solution was concentrated in vacuo. The residue was suspended in MeOH (5 mL), the precipitate was washed with MeOH, dried, and twice recrystallized from Pr<sup>i</sup>OH. The yield was 305 mg (26%), colorless crystals, m.p. 155-157 °C Found (%): C, 68.50; H, 7.02; Cl, 20.02; N, 4.03. C<sub>20</sub>H<sub>25</sub>Cl<sub>2</sub>N. Calculated (%): C, 68.57; H, 7.19; Cl, 20.24; N, 4.00. UV (MeCN),  $\lambda_{max}/nm$  ( $\epsilon/L$  mol<sup>-1</sup> cm<sup>-1</sup>): 282 (18300), 238 (8100), 210 (35000). IR (reflection), v/cm<sup>-1</sup>: 1521, 1556, 1601 (Ar), 2866, 2904, 2953 (CH<sub>3</sub>), 3041 (CH<sub>Ar</sub>), 3413 (NH). <sup>1</sup>H NMR, δ: 1.30 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>); 6.25 (s, 1 H, NH); 7.18 (dd, 2 H, H(5), J = 8.5 Hz, J = 2.2 Hz); 7.23 (d, 2 H, H(6), J = 8.5 Hz); 7.40 (d, 2 H, H(3), J = 2.2 Hz). <sup>13</sup>C NMR,  $\delta$ : 31.30 (CH<sub>2</sub>); 34.29 (C(CH<sub>2</sub>)); 117.43 (C(6)); 123.11 (C(2)); 124.32 (C(5)); 126.86 (C(3)); 136.47 (C(4)); 145.21 (C(1)).

<sup>1</sup>H—<sup>1</sup>H NOE: the enhancement of the NMR signals indicated the interaction of the protons CMe<sub>3</sub> ( $\delta$  1.30) with H(5) ( $\delta$  7.18), H(3) ( $\delta$  7.40). MS, *m/z* ( $I_{rel}$  (%)): 354 (1.10), 353 (5.61), 352 (7.01), 351 (32.33), 350 (11.51), 349 (47.95) [M]<sup>+</sup>, 339 (2.20), 338 (12.01), 337 (13.81), 336 (64.46), 335 (21.12), 334 (100) [M - CH<sub>3</sub>]<sup>+</sup>.

**B.** Dichloroamine 3 was also formed upon chlorination of amine-N-oxyl 1 in 35% yield. The spectral characteristics melting points of dichloroamine 3 obtained by methods A and B were identical.

N-(4-tert-Butyl-2,6-dichlorophenyl)-N-(4-tert-butyl-2-chlorophenyl)amine (4) was obtained upon chlorination of amine-Noxyl 1 in 34% yield. Colorless crystals, m.p. 121-122 °C (from Pr<sup>i</sup>OH). Found (%): C, 62.35; H, 6.37; Cl, 27.33; N, 3.50. C<sub>20</sub>H<sub>24</sub>Cl<sub>3</sub>N. Calculated (%): C, 62.43; H, 6.29; Cl, 27.64; N, 3.64. UV (MeCN),  $\lambda_{max}/nm$  ( $\epsilon/L$  mol<sup>-1</sup> cm<sup>-1</sup>): 278 (9500), 239 (14800), 205 (62600). IR (reflection), v/cm<sup>-1</sup>: 1485, 1509, 1551, 1573, 1611 (Ar), 2868, 2905, 2968 (CH<sub>3</sub>), 3041 (CH<sub>Ar</sub>), 3377 (NH). <sup>1</sup>H NMR, δ: 1.28 (s, 9 H, C(4<sup>2</sup>)(CH<sub>3</sub>)<sub>3</sub>); 1.33 (s, 9 H,  $C(4)(CH_3)_3$ ; 5.96 (s, 1 H, NH); 6.35 (d, 1 H, H(6'), J = 8.5 Hz); 7.07 (dd, 1 H, H(5'), J = 8.5 Hz, J = 2.3 Hz); 7.36 (d, 1 H, H(3'), J = 2.3 Hz; 7.39 (s, 2 H, H(3), H(5)). <sup>13</sup>C NMR,  $\delta$ : 31.07 (C(4')(CH<sub>3</sub>)); 31.35 (C(4)(CH<sub>3</sub>)); 34.13 (C(4')(CH<sub>3</sub>)); 34.81  $(C(4)(CH_3)); 114.35 (C(6')); 120.37 (C(2')); 124.06 (C(3'));$ 126.04 (C(3), C(5)); 126.35 (C(5')); 132.10 (C(2), C(6)); 133.26  $(C(4')); 137.73 (C(4)); 143.60 (C(1')); 150.38 (C(1)). {}^{1}H-{}^{1}H$ NOE: the enhancement of the NMR signals indicated the interaction of the following protons:  $C(4')(CH_3)_3 (\delta 1.28)$  with H(5') $(\delta 7.07)$  and H(3')  $(\delta 7.36)$ ; C(4)Me<sub>3</sub>  $(\delta 1.33)$  with H(3) and H(5) ( $\delta$  7.39). MS, m/z ( $I_{rel}$  (%)): 389 (1.20), 388 (2.70), 387  $(12.91), 386 (8.61), 385 (39.84), 384 (10.11), 383 (41.04) [M]^+,$ 374 (3.60), 373 (6.51), 372 (32.33), 371 (19.92), 370 (93.29), 369 (20.72), 368 (100) [M - CH<sub>3</sub>]<sup>+</sup>.

N-(4-tert-Butyl-2-chlorophenyl)-N-(2,4-dichlorophenyl)amine (5) was obtained upon chlorination of amine-N-oxyl 1 in 23% yield. Colorless crystals, m.p. 46 °C (from MeOH). Found (%): C, 58.46; H, 4.84; Cl, 32.54; N, 4.22. C<sub>16</sub>H<sub>16</sub>Cl<sub>3</sub>N. Calculated (%): C, 58.47; H, 4.91; Cl, 32.36; N, 4.26. UV (MeCN),  $\lambda_{max}/nm (\epsilon/L mol^{-1} cm^{-1}): 284 (20600), 242 (8000), 209 (41000).$ IR (reflection), v/cm<sup>-1</sup>: 1482, 1494, 1520, 1593 (Ar), 2870, 2906, 2969 (CH<sub>3</sub>), 3058 (CH<sub>AT</sub>), 3402 (NH). <sup>1</sup>H NMR, δ: 1.31 (s, 9 H,  $C(CH_3)_3$ ; 6.26 (s, 1 H, NH); 7.11 (dd, 1 H, H(5), J = 8.8 Hz, J = 2.3 Hz; 7.15 (d, 1 H, H(6), J = 8.8 Hz); 7.22 (m, 2 H, H(5'), H(6'); 7.39 (d, 1 H, H(3), J = 2.3 Hz); 7.42 (m, 1 H, H(3')). <sup>13</sup>C NMR,  $\delta$ : 31.25 (CH<sub>3</sub>); 34.41 (<u>C</u>(CH<sub>3</sub>)<sub>3</sub>); 117.10 (C(6)); 119.02 (C(6<sup>^</sup>)); 123.02 (C(2<sup>^</sup>)); 124.47 (C(2)); 124.51 (C(5<sup>^</sup>)); 125.13 (C(4)); 127.11 (C(3')); 127.49 (C(5)); 129.45 (C(3));  $135.40 (C(4')); 138.33 (C(1')); 146.69 (C(1)). {}^{1}H-{}^{1}H NOE: the$ enhancement of the NMR signals indicated the interaction of the protons  $C(CH_3)_3$  ( $\delta$  1.31) with H(3') ( $\delta$  7.42) and H(5') $(\delta 7.22)$ . MS,  $m/z (I_{rel} (\%))$ : 331 (10.01), 330 (4.10), 329 (33.63), 328 (5.51), 327 (35.94) [M]<sup>+</sup>, 316 (29.43), 315 (14.41), 314 (98.60),  $313(17.02), 312(100) [M - CH_3]^+.$ 

Bis(4-*tert*-butyl-2,6-dichlorophenyl)amine (6) was obtained upon chlorination of amine-*N*-oxyl 1 in 2% yield. Colorless crystals, m.p. 227–228 °C (from Pr<sup>i</sup>OH). Found (%): C, 57.19; H, 5.47; Cl, 33.53; N, 3.30. C<sub>20</sub>H<sub>23</sub>Cl<sub>4</sub>N. Calculated (%): C, 57.30; H, 5.53; Cl, 33.83; N, 3.34. UV (MeCN),  $\lambda_{max}/nm$ (ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 281 (15700), 241sh (10400), 206 (50000). IR (reflection), v/cm<sup>-1</sup>: 1499, 1510, 1549, 1561, 1599 (Ar), 2872, 2905, 2965 (CH<sub>3</sub>), 3396 (NH). <sup>1</sup>H NMR, δ: 1.29 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>); 5.73 (s, 1 H, NH); 7.25 (s, 4 H, H(3), H(5)). <sup>1</sup>H $^{-1}$ H NOE: the enhancement of the NMR signals indicated the interaction of the protons C(CH<sub>3</sub>)<sub>3</sub> ( $\delta$  1.29) with H(3), H(5) ( $\delta$  7.25). MS, *m*/*z* (*I*<sub>rel</sub> (%)): 421 (6.01), 420 (2.20), 419 (13.61), 418 (2.40), 417 (10.11) [M]<sup>+</sup>, 408 (2.00), 407 (2.10), 406 (13.91), 405 (5.31), 404 (27.33), 403 (4.00), 402 (22.72) [M - CH<sub>3</sub>]<sup>+</sup>.

N-(4-tert-Butyl-2,6-dichlorophenyl)-N-(2´,4´-dichlorophenyl)amine (7) was obtained upon chlorination of amine-N-oxyl 1 in 2% yield. A colorless resin. Found (%): C, 52.99; H, 4.11; Cl, 38.95; N, 4.11. C<sub>16</sub>H<sub>15</sub>Cl<sub>4</sub>N. Calculated (%): C, 52.92; H, 4.16; Cl, 39.05; N, 3.86. UV (MeCN),  $\lambda_{max}/nm$  ( $\epsilon/L$  mol<sup>-1</sup> cm<sup>-1</sup>): 276 (10000), 246 (13000), 204 (61900). IR (reflection), v/cm<sup>-1</sup>: 1496, 1550, 1590 (Ar), 2872, 2907, 2967 (CH<sub>3</sub>), 3081 (CH<sub>Ar</sub>), 3391 (NH). <sup>1</sup>H NMR, δ: 1.33 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>); 5.97 (s, 1 H, NH); 6.31 (d, 1 H, H(6), J = 8.7 Hz); 7.02 (dd, 1 H, H(5)), J = 8.8 Hz, J = 2.4 Hz); 7.35 (d, 1 H, H(3'), J = 2.3 Hz); 7.40 (s, 2 H, H(3), H(5)). <sup>13</sup>C NMR, δ: 31.02 (CH<sub>3</sub>); 34.87 (C(CH<sub>3</sub>)<sub>3</sub>); 115.06 (C(6')); 120.90 (C(2')); 124.19 (C(4')); 126.16 (C(3), C(5)); 127.26 (C(3')); 128.94 (C(5')); 132.31 (C(4)); 132.45  $(C(2), C(6)); 139.17 (C(1)); 151.16 (C(1')). {}^{1}H-{}^{1}H \text{ NOE: the}$ enhancement of the NMR signals indicated the interaction of protons C(CH<sub>3</sub>)<sub>3</sub> ( $\delta$  1.33) with H(3), H(5) ( $\delta$  7.40). MS, m/z $(I_{rel} (\%))$ : 367 (4.80), 366 (3.70), 365 (25.33), 364 (9.31), 363 (51.85), 362 (7.81), 361 (40.74) [M]<sup>+</sup>, 352 (9.61), 351 (7.11), 350 (47.65), 349 (16.82), 348 (100), 347 (15.42), 346 (77.68)  $[M - CH_3]^+$ .

*N*-(4'*-tert*-Butyl-2'*-*chlorophenyl)-*N*-(2,4,6-trichlorophenyl)amine (8) was obtained upon chlorination of amine-*N*-oxyl 1 in a mixture with tetrachloroamine 7. <sup>1</sup>H NMR, 8: 1.28 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>); 5.96 (s, 1 H, NH); 6.32 (d, 1 H, H(6'), J = 8.5 Hz); 7.08 (dd, 1 H, H(5'), J = 8.5 Hz, J = 2.2 Hz); 7.37 (d, 1 H, H(3')), J = 2.2 Hz); 7.41 (s, 2 H, H(3), H(5)). <sup>13</sup>C NMR, 8: 31.31 (CH<sub>3</sub>); 34.15 (<u>C</u>(CH<sub>3</sub>)<sub>3</sub>); 114.64 (C(6')); 120.90 (C(2')); 124.07 (C(5')); 126.50 (C(3')); 128.75 (C(3), C(5)); 130.68 (C'(4)); 132.63 (C(2), C(6)); 135.06 (C(4')); 136.88 (C(1')); 144.38 (C(1)). <sup>1</sup>H-<sup>1</sup>H NOE: the enhancement of the NMR signals indicated the interaction of the protons C(CH<sub>3</sub>)<sub>3</sub> (81.28) with H(3') (87.37), H(5') (87.08).

**Bis(2,4-dichlorophenyl)amine (9)** was obtained upon chlorination of amine-*N*-oxyl 1 in 1.5% yield. Colorless crystals, m.p. 141.5 °C (from MeCN); *cf.* Ref. 10: m.p. 141–142 °C. UV (MeCN),  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/L$  mol<sup>-1</sup> cm<sup>-1</sup>): 289 (19700), 246 (8700), 209<sub>sh</sub> (39000). IR (reflection),  $\nu/\text{cm}^{-1}$ : 1470, 1516, 1591 (Ar), 3082, 3091 (CH<sub>Ar</sub>), 3398 (NH). <sup>1</sup>H NMR,  $\delta$ : 6.28 (s, 1 H, NH); 7.16 (m, 4 H, H(5), H(6)); 7.42 (m, 2 H, H(3)). <sup>13</sup>C NMR,  $\delta$ : 118.60 (C(6)); 124.41 (C(2)); 126.68 (C(4)); 127.70 (C(5)); 129.78 (C(3)); 137.31 (C(1)). MS, *m/z* (*I*<sub>rel</sub> (%)): 311 (7.51), 310 (3.70), 309 (47.55), 308 (12.51), 307 (100), 306 (3.30), 305 (77.88) [M]<sup>+</sup>.

Bis(4-*tert*-butylphenyl)amine hydrochloride (10 · HCl) was formed as a precipitate in the chlorination of amine 10 in CCl<sub>4</sub>. Colorless crystals, m.p. 136–138 °C (from MeCN). Found (%): C, 75.23; H, 8.63; Cl, 10.99; N, 4.38. C<sub>20</sub>H<sub>27</sub>N · HCl. Calculated (%): C, 75.56; H, 8.88; Cl, 11.15; N, 4.41. UV (MeCN),  $\lambda_{max}/nm$  (ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 286 (24400), 241 (5500). IR (reflection), v/cm<sup>-1</sup>: 1511, 1559, 1609 (Ar), 1999, 2041, 2203, 2359, 2384, 2492, 2571 (NH<sub>2</sub>), 2869, 2906, 2964 (CH<sub>3</sub>), 3063 (CH<sub>Ar</sub>).

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