Supplementary Material

Synthesis and spectral comparison of electronic and molecular properties of some hydrazines and hydrazyl free radicals

Bianca Patrascu, Cecilia Lete, Codruta Popescu, Mihaela Matache, Anca Paun, Augustin Madalan, and Petre Ionita*

*University of Bucharest, Faculty of Chemistry, Panduri 90-92, Bucharest, Romania
b) Institute of Physical Chemistry, 202 Spl. Independentei, Bucharest, Romania
Email: petre.ionita@chimie.unibuc.ro

Table of Contents

Compound 5a: Crystallographic data, details of data collection and structure refinement parameters (Table S1) .................................................................................................................................................. S2
Selected bond lengths from X-ray (Table S2) .......................................................................................................................................................................................... S3
Compounds 1-5: Main parameters for calculation of standard constants (Table S3) .................................................................................................................. S4
Compound 4a: IR spectrum: trace (Figure S1) ............................................................................................................................................................................. S5
1H NMR spectrum: trace (Figure S2) ............................................................................................................................................................................. S5
13C NMR spectrum: trace (Figure S3) ............................................................................................................................................................................. S6
UV/Vis spectra traces of hydrazines 1a-5a and their anions 1c-5c (Figure S4) ..................................................................................................................... S7
UV/Vis spectra traces of free radicals 1b-5b (Figure S5) ..................................................................................................................................................... S7
Cyclic voltammetry of the anions 1c-5c (Figure S6) ..................................................................................................................................................... S8
**Table S1.** Crystallographic data, details of data collection and structure refinement parameters for compound 5a.

| Parameter                        | Value                      |
|----------------------------------|----------------------------|
| Chemical formula                 | C₁₈H₁₁N₅O₆                 |
| $M$ (g mol⁻¹)                    | 393.32                     |
| Temperature, (K)                 | 293(2)                     |
| Wavelength, (Å)                  | 0.71073                    |
| Crystal system                   | Monoclinic                 |
| Space group                      | $P2_1/a$                   |
| $a$ (Å)                          | 10.0415(7)                 |
| $b$ (Å)                          | 24.5824(15)                |
| $c$ (Å)                          | 14.6763(14)                |
| $\alpha$ (°)                    | 90                         |
| $\beta$ (°)                     | 107.858(6)                 |
| $\gamma$ (°)                    | 90                         |
| $V$ (Å³)                         | 3448.2(5)                  |
| $D_c$ (g cm⁻³)                   | 1.515                      |
| $\mu$ (mm⁻¹)                    | 0.118                      |
| $F(000)$                         | 1616                       |
| Goodness-of-fit on $F^2$         | 0.998                      |
| Final $R_1, wR_2$                | 0.0477, 0.1160             |
| Final $R_1, wR_2$ [I>2$\sigma$(I)] | 0.0477, 0.1160             |
| $R_1$, $wR_2$ (all data)        | 0.0949, 0.1364             |
| Largest diff. peak and hole (eÅ⁻³) | 0.245, -0.225              |
Table S2. Selected bond lengths (Å) for the compound 5a.

| Bond    | Length | Bond    | Length | Bond    | Length |
|---------|--------|---------|--------|---------|--------|
| C1-C2   | 1.373(3)| C19-C20 | 1.370(3)| N1-N2   | 1.378(2) |
| C1-N1   | 1.393(2)| C19-C24 | 1.387(3)| N2-H2N  | 0.86(2)  |
| C1-C6   | 1.397(2)| C19-N6  | 1.401(2)| N3-O1   | 1.217(2) |
| C2-C3   | 1.381(3)| C20-C21 | 1.375(3)| N3-O2   | 1.219(2) |
| C3-C4   | 1.388(3)| C21-C22 | 1.373(4)| N4-O3   | 1.209(2) |
| C4-C5   | 1.368(3)| C22-C23 | 1.353(4)| N4-O4   | 1.209(2) |
| C5-C6   | 1.392(3)| C23-C24 | 1.404(3)| N5-O5   | 1.221(3) |
| C6-C7   | 1.449(3)| C24-C25 | 1.438(3)| N5-O6   | 1.223(3) |
| C7-C8   | 1.388(3)| C25-C26 | 1.391(3)| N6-N7   | 1.377(2) |
| C7-C12  | 1.397(3)| C25-C30 | 1.395(3)| N7-H1N  | 0.88(2)  |
| C8-C9   | 1.373(4)| C26-C27 | 1.359(4)| N8-O8   | 1.213(2) |
| C9-C10  | 1.380(4)| C27-C28 | 1.370(4)| N8-O7   | 1.2214(19)|
| C10-C11 | 1.384(3)| C28-C29 | 1.401(4)| N9-O10  | 1.213(2) |
| C11-C12 | 1.382(3)| C29-C30 | 1.387(3)| N9-O9   | 1.225(2) |
| C12-N1  | 1.396(2)| C30-N6  | 1.389(3)| N10-O12 | 1.205(3) |
| C13-N2  | 1.346(3)| C31-N7  | 1.353(2)| N10-O11 | 1.230(3) |
| C13-C18 | 1.416(3)| C31-C36 | 1.411(3)|         |         |
| C13-C14 | 1.419(2)| C31-C32 | 1.421(3)|         |         |
| C14-C15 | 1.375(3)| C32-C33 | 1.371(3)|         |         |
| C14-N3  | 1.468(2)| C32-N8  | 1.457(2)|         |         |
| C15-C16 | 1.370(3)| C33-C34 | 1.364(3)|         |         |
| C16-C17 | 1.370(3)| C34-C35 | 1.376(3)|         |         |
| C16-N4  | 1.450(3)| C34-N9  | 1.462(2)|         |         |
| C17-C18 | 1.360(3)| C35-C36 | 1.363(3)|         |         |
| C18-N5  | 1.472(3)| C36-N10 | 1.474(3)|         |         |
Table S3. Main parameters for calculation of standard rate constants of 1c-5c.

| Compound | $\Delta E_p$ (mV) | $\Psi$ | $K^o$ (cm/s) |
|----------|-------------------|--------|--------------|
| 1c       | 90                | 0.75   | 0.182        |
| 2c       | 150               | 0.25   | 0.061        |
| 3c       | 90                | 0.75   | 0.182        |
| 4c       | 90                | 0.75   | 0.182        |
| 5c       | 80                | 1      | 0.242        |
**Figure S1.** IR spectrum of the new compound 4a.
**Figure S2.** $^1$H-NMR of the new compound 4a.

![$^1$H-NMR spectrum of compound 4a](image1)

**Figure S3.** $^{13}$C-NMR of the new compound 4a.

![$^{13}$C-NMR spectrum of compound 4a](image2)
**Figure S4.** UV-Vis spectra of the hydrazines 1a-5a (blue) and their anions 1c-5c (red).

**Figure S5.** UV-Vis spectra of the free radicals 1b-5b.
**Figure S6.** Cyclic voltammetry of the anions 1c-5c.