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# Molecular and crystal structure of 5,6-diamino-1-methyluracil and 5,6-diamino-1,3-dimethyluracil monohydrate. Semiempirical calculations (AM1 and PM3) on 5,6-diaminouracil derivatives

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# Abstract

The crystal and molecular structures of 5,6-diamino-1-methyluracil and 5,6-diamino-1,3-dimethyluracil monohydrate have been determined from X-ray diffraction. Both compounds are planar and the two amino groups have two different conformations. The substituent at the 5 position seems to be a true primary amino group with a strongly  $sp^3$  nitrogen, whereas the one at the 6 position is nearly coplanar with the uracil ring, displaying a predominant  $sp^2$  character.

Semiempirical calculations were made on 5,6-diaminouracil, 5,6-diamino-2-thiouracil and their endocyclic *N*-methylated derivatives using the AM1 and PM3 hamiltonians. These indicate that the stability decreases on increasing methylation, the 2-thio compounds always being less stable than the 2-oxo ones. © 1997 Elsevier Science B.V.

Keywords: X-ray crystallography; Semiempirical calculations; 5,6-diaminouracil derivatives

### 1. Introduction

The structural study of these 5,6-diaminouracil derivatives is a part of a series of X-ray analyses of various 6-aminouracil derivatives (such as 5-unsubstituted [1,2], 5-formyl and 5-nitroso [3,4], 5-hydroxyiminomethyl [5,6] and 5-diazo [7,8]) carried out in order to determine the nature of their hydrogen bonding and molecular geometry because of our interest in the coordination behaviour of these 6-aminouracil analogs [9–20]. The comparison of the structure of free and coordinated uracil ligands is of importance in the determination of what happens to the electronic densities and bond orders upon coordination, which may clarify the discussions of results about other experimental data, mainly vibrational spectra. Semiempirical studies may be of utility in predicting the coordination and acid-base features of a potentially ambidentate ligand, such as the above-cited uracil derivatives. Molecular orbital calculations have been used to determine which of the available atoms must be the main donor atom, this being a better method for this purpose than the analysis of either net charge on the atoms or electrostatic potentials [12,21,22].

We have found no references to either the crystal structures or coordinating properties of 5,6-diaminouracil derivatives. These compounds may act as precursors of *N*-oxide compounds [23,24] which

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|                                  |        | X | R,  | R,  |
|----------------------------------|--------|---|-----|-----|
| 0                                | AAU    | 0 | н   | н   |
| Ŷ                                | 1MAAU  | 0 | СН₃ | н   |
| R <sub>3</sub> N NH <sub>2</sub> | 3MAAU  | 0 | н   | CH3 |
|                                  | DAAU   | 0 | CH3 | СН₃ |
| X N NH                           | TAAU   | S | н   | н   |
| P 2                              | T1MAAU | S | CH3 | н   |
| 11                               | T3MAAU | S | н   | Сн₃ |
|                                  | TDAAU  | S | СН3 | CH3 |

Fig. 1. Molecular structure of the studied compounds.

have important photochemical properties. The influence of metal ions in the oxidation of these conjugated  $\alpha$ -carbonyl-enediamine systems has also been reported [25].

The crystal and molecular structures of two 5,6diaminouracil derivatives and a theoretical study, from semiempirical methods AM1 and PM3, of the donor properties of the set of related compounds drawn in Fig. 1 are reported here.

# 2. Experimental section

# 2.1. Synthesis

The 6-aminouracil derivatives may be obtained by condensation of the corresponding methylurea with cyanoacetic acid. These were reacted with the stoichiometric amounts of sodium nitrite and acetic acid to give both 6-amino-5-nitrosouracil derivatives. The reduction of these with ammonium sulfide yields the powdered title compounds. On recrystallizing them from water, light yellow needles of both compounds may be obtained. Elemental analysis indicates that DAAU crystallizes as the monohydrate. Analyses were: 1MAAU; Found: C, 38.27; H, 5.85; N, 35.22%; Calcd.: C, 38.45; H, 5.17; N, 35.88%. DAAU; Found: C, 38.09; H, 6.25; N, 29.19%; Calcd.: C, 38.28; H, 6.44; N, 29.77%.

# 2.2. Crystallographic work

Colorless crystals of the title compounds were mounted on a Nonius CAD4 diffractometer with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda =$ 0.7107 Å). The unit cells were determined from 25 randomly oriented reflections. The intensity data were collected with the  $\omega - 2\theta$  scan mode. Three standard reflections were monitored every 120 min with intensity decays of 1.5% (1MAAU) and 1.0% (DAAU). The structures were solved by direct methods and refined by full-matrix least-squares on *F* and a weighting scheme  $w = 1/[\sigma^2(F_0^2) + (xP)^2]$ , where  $P = 1/3(F_0^2 + 2F_c^2)$ , x = 0.0573 (1MAAU) and x = 0.0849 (DAAU). Other experimental details are given in Table 1. Data reduction was performed with DATRD2 in NRCVAX [26], structure solving with SHELXS86 [27], structure refinement with NRCVAX94 and SHELXL93 [28]. Molecular graphics and geometrical calculations were made with ORTEP [29], PLUTON [30] and PLATON [31].

# 2.3. Semiempirical calculations

Semiempirical calculations were performed for the 5,6-diaminouracil, 5,6-diamino-2-thiouracil and their endocyclic N-methylated derivatives using the AM1 and PM3 hamiltonians as implemented in the HYPERCHEM 4.0 package. All calculations have been carried out at the RHF level for the singlet lowest energy state with no configuration interaction. The molecular structures have been generated with the molecular builder inside HYPERCHEM and optimized following the Polak-Ribiere algorithm until a RMS gradient of 0.001 kcal  $Å^{-1}$  mol<sup>-1</sup>. In order to check the goodness of the resulting structures the infrared spectrum has been also calculated, the non-appearance of negative frequencies being assumed as unequivocal evidence that each structure represents a global potential energy minimum not a local minimum. For this purpose, it was not necessary to introduce either geometrical or conformational restrictions in the starting models.

| Table 1      |      |     |     |                  |          |  |
|--------------|------|-----|-----|------------------|----------|--|
| Experimental | data | for | the | crystallographic | analysis |  |

|  | 1MAAU   | DAAU                           |  |  |
|--|---|--------------------------------|--|--|
| Formula  | C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub> | $C_{6}H_{10}N_{4}O_{2}H_{2}O$  |  |  |
| Color, habit                                       | Colorless, block  | Colorless, block               |  |  |
| Formula weight                                     | 156.15  | 188.20                         |  |  |
| Crystal system                                     | Monoclinic  | Monoclinic                     |  |  |
| Space group  | $P2_1/n$  | $P2_1/c$                       |  |  |
| Temperature, K                                     | 294(1)  | 294(1)                         |  |  |
| Refins. for lattice param.                         | $25 (9.50 < \theta < 16.50)$                                | $25 (9.50 < \theta < 16.50)$   |  |  |
| a, Å   | 7.6410(6)   | 7.5034(6)                      |  |  |
| b, Å   | 7.6026(6)   | 11.5512(6)                     |  |  |
| <i>c</i> , Å                                       | 11.6529(9)  | 10.1079(9)                     |  |  |
| β,°  | 107.937(7)  | 103.165(7)                     |  |  |
| Volume, Å <sup>3</sup>                             | 644.03(9)   | 853.1(1)                       |  |  |
| Z  | 4   | 4                              |  |  |
| Density (calc.), Mg m <sup>-3</sup>                | 1.610   | 1.465                          |  |  |
| $\mu$ , mm <sup>-1</sup>                           | 0.128   | 0.118                          |  |  |
| F(000)   | 328   | 400                            |  |  |
| Exp. absorption correction                         | None  | None                           |  |  |
| Crystal size, mm <sup>3</sup>                      | $0.39 \times 0.28 \times 0.23$                              | $0.36 \times 0.35 \times 0.27$ |  |  |
| Measured reflections                               | 1503  | 1989                           |  |  |
| Indexes range h                                    | - 9 to 9  | - 9 to 9                       |  |  |
| k  | 0 to 9  | 0 to 14                        |  |  |
| 1  | 0 to 14   | 1 to 12                        |  |  |
| $\theta$ range, °                                  | 2.83-26.91  | 2.71-26.90                     |  |  |
| Independent reflections                            | 1406  | 1856                           |  |  |
| Observed reflect. $(I > 2\sigma(I))$               | 1088  | 1366                           |  |  |
| Number of refined parameters                       | 107   | 132                            |  |  |
| R (all, obs. data)                                 | 0.0498, 0.0353  | 0.0605, 0.0437                 |  |  |
| Final wR (all, obs. data)                          | 0.2047, 0.1010  | 0.1496, 0.1426                 |  |  |
| Goodness of fit (all, obs.)                        | 1.264, 1.401  | 1.309, 1.472                   |  |  |
| Largest $\Delta/\sigma$                            | -0.008  | 0.027                          |  |  |
| Max. dens. final $\Delta F$ map, e Å <sup>-3</sup> | + 0.191   | + 0.293                        |  |  |
| Min. dens. final $\Delta F$ map, e Å <sup>-3</sup> | - 0.198   | - 0.223                        |  |  |

# 3. Results and discussion

# 3.1. Structural study

Final atomic coordinates as determined from X-ray diffraction are shown in Table 2 and a view of the molecule with the atom numbering scheme is displayed in Fig. 2. Interatomic distances and angles are listed in Table 3.

Both molecules are practically planar within 0.02 Å for endocyclic atoms and 0.1 Å for the exocyclic ones. Distances and angles are very close to those found in other 6-aminouracil derivatives [2–6] indicating a great electronic delocalization in the uracil ring. The major structure feature is the difference found between the 5-amino and 6-amino groups. The former

is a true primary amino group in which the valence orbitals of nitrogen atom seem to have a strong  $sp^3$ character. One of the hydrogen atoms lies close to the plane of the ring since it is involved in an intramolecular hydrogen bond with the adjacent atom O4 in each molecule. The second of these atoms lies out of the plane of the ring and, unusually, is not involved in hydrogen bonding in 1MAAU compound. The hydrogen atoms of the 6-amino group were clearly revealed in difference maps to be coplanar with the rest of the molecule, the N6 atom displaying a predominantly sp<sup>2</sup> character as found in other 6-aminouracil compounds [2-6]; the AFIX 93 command in SHELXL93 was used for these atoms. A delocalization of the nitrogen  $\pi$ -lone pair in the ring results in a shorter C-N distance (ca. 7%) due to the higher Table 2

| Atom  | x/a     | y/b        | zlc       | Uiso   |  |
|-------|---------|------------|-----------|--------|--|
| IMAAU |         | - <u>.</u> |           |        |  |
| N1    | 2562(2) | 1068(1)    | 596(1)    | 255(3) |  |
| Cl    | 1714(2) | 2818(2)    | 382(1)    | 335(3) |  |
| C2    | 3674(2) | 678(2)     | 1745(1)   | 271(3) |  |
| O2    | 3893(2) | 1710(1)    | 2592(1)   | 394(3) |  |
| N3    | 4531(2) | - 905(2)   | 1888(1)   | 290(3) |  |
| C4    | 4367(2) | - 2165(2)  | 1002(1)   | 259(3) |  |
| O4    | 5256(1) | - 3563(1)  | 1273(1)   | 367(3) |  |
| C5    | 3173(2) | - 1737(2)  | - 148(1)  | 240(3) |  |
| N5    | 2832(2) | - 2994(2)  | - 1106(1) | 295(3) |  |
| C6    | 2269(2) | - 145(2)   | - 340(1)  | 235(3) |  |
| N6    | 1110(2) | 307(2)     | - 1414(1) | 327(3) |  |
| DAAU  |         |            |           |        |  |
| N1    | 6966(2) | 376(1)     | 9318(1)   | 373(3) |  |
| Cl    | 6125(3) | 1221(2)    | 8280(2)   | 508(5) |  |
| C2    | 6752(2) | - 775(1)   | 8974(1)   | 378(4) |  |
| O2    | 5883(2) | - 1098(1)  | 7857(1)   | 542(4) |  |
| N3    | 7571(2) | - 1553(1)  | 9952(1)   | 393(4) |  |
| C3    | 7311(3) | - 2794(2)  | 9653(2)   | 565(5) |  |
| C4    | 8682(2) | - 1240(1)  | 11210(1)  | 366(4) |  |
| 04    | 9430(2) | - 2007(1)  | 11998(1)  | 515(4) |  |
| C5    | 8843(2) | - 49(1)    | 11500(2)  | 363(4) |  |
| N5    | 9829(2) | 300(1)     | 12820(1)  | 444(4) |  |
| C6    | 7980(2) | 754(1)     | 10570(1)  | 346(4) |  |
| N6    | 8091(2) | 1888(1)    | 10810(2)  | 488(4) |  |
| O3    | 2781(2) | - 919(2)   | 5582(1)   | 644(4) |  |

Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^4 \text{ Å}^2$ ) for non-hydrogen atoms, with esd's in parentheses

imino character of the 6-amino group, as compared with the 5-amino group. These facts are in accord with the chemical behaviour of both groups; the 5-amino groups reacts as a primary amino group, whereas the 6-amino group does not. This suggests that the coordination ability must be higher for the 5-amino group than for the 6-amino one. In addition, like other uracil derivatives [2-6], the C2=O2 carbonyl group is a little shorter than the C4=O4 one, showing once more that the more stable tautomer for these uracil derivatives is the dicarbonylic form. Puckering analysis using PLATON program [31] indicates that the base rings in both compounds are not puckered.

Fig. 3 shows a view of the hydrogen bonds established in these compounds and, in Table 4, the complete details of these interactions are given.

The molecules in compound 1MAAU form a complex three-dimensional hydrogen bonded network consisting of two interpenetrating sheets of molecules. An almost planar base-paired unit is formed by two centrosymmetrically related molecules forming N5-H···O4 bonds, 3.033(2) Å. These units are linked to similar units via a N6-H...O2 bond, 2.854(2) Å, to form a two-dimensional infinite sheet. In addition, each molecule base-pairs to screw-related molecules via N3-H···N5 and N6-H···O4 hydrogen bonds (2.982(2) and 2.892(2) Å, respectively). The molecules involved here are highly twisted with respect to each other but form an infinite chain. However, each molecule is already in the previously described planar sheets and this twist results in the creation of two sheets angled with respect to each other. Thus, the whole structure consists of an infinite series of hydrogen-bonded interpenetrating sheets. Examination of the structure with PLATON [31] showed that there were no solvent accessible voids in the crystal lattice.

In DAAU, the water molecule (O3) lies 0.75(2) Å from the mean plane of the uracil moiety and is hydrogen bonded to it via O2 (O3-H···O2, 2.883(2) Å). These units are then hydrogen bonded to other such units forming infinite two-dimensional sheets which



Fig. 2. ORTEP drawings and atom numbering scheme of the 5,6diamino-1-methyluracil (top) and 5,6-diamino-1,3-dimethyluracil monohydrate (bottom). Ellipsoids are shown at 50% probability.

lie in the  $[-1\ 0\ 1]$  plane and run parallel to the *b* axis. These sheets are linked to each other by the single O3-H…N5 hydrogen bond (2.898 (2) Å). Once again bases stack above each with the closest interatomic separations greater than 3.5 Å.

Table 3 Interatomic distances  $(\text{\AA})$  and angles (°) for non-hydrogen atoms with esd's in parentheses

| IMAAU    | DAAU  |
|----------|---|
| 1.467(2) | 1.467(2)  |
| 1.379(2) | 1.374(2)  |
| 1.393(2) | 1.390(2)  |
| 1.232(2) | 1.227(2)  |
| 1.356(2) | 1.373(2)  |
| 1.385(2) | 1.399(2)  |
| 1.248(2) | 1.237(2)  |
| 1.407(2) | 1,406(2)  |
| 1.431(2) | 1.428(2)  |
| 1.377(2) | 1.374(2)  |
| 1.336(2) | 1.331(2)  |
|          | 1.469(2)  |
| 117.9(1) | 117.2(1)  |
| 120.7(1) | 119.9(1)  |
| 121.4(1) | 122.8(1)  |
| 122.1(1) | 122.2(1)  |
| 116.1(1) | 116.3(1)  |
| 121.6(1) | 121.4(2)  |
| 126.4(1) | 124.2(1)  |
| 118.9(1) | 119.3(1)  |
| 115.7(1) | 116.6(1)  |
| 125.5(1) | 124.1(1)  |
| 119.9(1) | 118.2(1)  |
| 120.2(1) | 120.9(1)  |
| 119.9(1) | 120.8(1)  |
| 120.2(1) | 119.1(1)  |
| 117.6(1) | 118.3(1)  |
| 122.2(1) | 122.7(1)  |
|          | 118.3(1)  |
|          | 117.6(1)  |
|          | 1MAAU   1.467(2)   1.379(2)   1.393(2)   1.232(2)   1.356(2)   1.385(2)   1.4431(2)   1.477(2)   1.336(2)   117.9(1)   120.7(1)   121.4(1)   122.1(1)   116.1(1)   121.6(1)   126.4(1)   118.9(1)   115.7(1)   122.5(1)   119.9(1)   120.2(1)   117.6(1)   122.2(1) |

In both compounds, there are two intramolecular hydrogen bonding interactions, one between N5 and O4, the other is between N6 and N5. In DAAU, all possible donor hydrogen atoms are involved in hydrogen bonding interactions whereas in 1MAAU, the outof-plane hydrogen attached to N5, as mentioned above, is not involved in any interaction.

A comparison between the geometries of experimental XRD structures and the optimized ones, obtained from the semiempirical calculations, shows that bond lengths obtained from AM1 and PM3 semiempirical methods are overestimated at around 0.03 Å (rms = 0.03-0.04 Å) for both uracil derivatives. In addition, a mean deviation from 1.2 to 1.5° for the angles (rms =  $1.5-1.9^{\circ}$ ) and a mean deviation between 2.7 and 9.4° (rms from 3.4 to 11.1°) for the torsions, have been found. It is important to note that the



Fig. 3. View of the hydrogen bonds: 1MAAU (top) and DAAU (bottom).

| Table 4          |                    |
|------------------|--------------------|
| Geometrical data | for hydrogen bonds |

| D-H···A                                    | D–H, Å | H…A, Å | D…A, Å   | D−H…A, ° |
|--|--------|--------|----------|----------|
| IMAAU                                      |        |        |          |          |
| N5-H51O4 $(x, y, z)$                       | 0.86   | 2.45   | 2.853(2) | 110      |
| N6-H61N5 $(x, y, z)$                       | 0.86   | 2.49   | 2.805(2) | 103      |
| N3-H3····N5 $(1/2 + x, -1/2 - y, 1/2 + z)$ | 0.86   | 2.18   | 2.982(2) | 154      |
| N5-H51···O4 $(1 - x, -1 - y, -z)$          | 0.86   | 2.27   | 3.033(2) | 148      |
| N6-H62···O2 $(x - 1/2, 1/2 - y, z - 1/2)$  | 0.86   | 2.04   | 2.854(2) | 156      |
| N6-H61···O4 $(x - 1/2, -1/2 - y, z - 1/2)$ | 0.86   | 2.06   | 2.892(2) | 163      |
| DAAU                                       |        |        |          |          |
| N5-H51····O4 $(x, y, z)$                   | 0.86   | 2.36   | 2.787(2) | 111      |
| N6-H61N5 $(x, y, z)$                       | 0.86   | 2.52   | 2.826(2) | 102      |
| N5-H52···O4 $(2 - x, 1/2 + y, 2 1/2 - z)$  | 0.86   | 2.38   | 3.159(2) | 151      |
| N6-H61···O4 $(2 - x, 1/2 + y, 2 1/2 - z)$  | 0.86   | 2.01   | 2.850(2) | 163      |
| N6-H62···O3 $(1 - x, 1/2 + y, 1 1/2 - z)$  | 0.86   | 2.13   | 2.899(2) | 149      |
| $O3-H34\cdots N5 (1-x, -y, 2-z)$           | 0.82   | 2.08   | 2.898(2) | 174      |
| $O3-H35\cdots O2(x, y, z)$                 | 0.82   | 2.15   | 2.883(2) | 148      |

generated structures simulate to a good degree the differences found between the two amino groups, but do assign the N6 atom a higher  $sp^3$  (or less  $sp^2$ ) character than that found by X-ray diffraction, implying a lower electronic delocalization of the nitrogen lone pair. The calculated C6-N6 distance is still shorter than the C5-N5 one but too large if compared with the X-ray diffraction data. The small differences found between both carbonylic bonds are not shown at all in the semiempirical generated structures. Taking into account the differences resulting from the different conditions in which X-ray diffraction experiment and semiempirical calculations are carried out, such as the absence of intermolecular interactions and the differences in bond lengths between calculated internuclear distances and those found by refined electronic densities measurements, the analysis of all geometrical data indicates that experimental structures are slightly better simulated by means of the AM1 semiempirical method than the PM3 one.

# 3.2. Molecular orbital calculations

In order to evaluate the relative stabilities and their potential coordinative properties, molecular orbital calculations have been performed for 5,6-diaminouracil, 5,6-diamino-2-thiouracil and their endocyclic *N*-methylated derivatives in their more stable dicarbonylic tautomeric form. We have obtained two optimized structures (AM1 and PM3) for all the studied compounds. The planarity of the generated structures is slightly lower than that of X-ray structures, the greater deviations being for N6 (AM1) and N6 and O2/S2 atoms (PM3).

The binding energies, heats of formation and dipole moments are given in Table 5. In each set of data (2-oxo and 2-thio compounds), it is clearly shown that on methylation the formation is unfavoured, the stability of N1- and N3-methylated derivatives being, in each set, very close. Clear differences may be observed between the 2-oxo and 2-thio compounds, the latter displaying a heat of formation which is slightly positive. This fact must clearly attributed to the weaker character of the C=S bond if compared with C=O bond, the energy difference between them being ca. 50 (AM1) and ca. 65 kcal mol<sup>-1</sup> (PM3).

For each set, dipole moments increase in the order 3-methyl < 1,3-dimethyl < unmethylated < 1-methyl. For analogous structures, the dipole moment of the 2-thio derivative is always greater than that for the 2-oxo derivative, which may be related with the higher size of the sulfur-containing compounds than that for the 2-oxo compounds.

On the other hand, the analysis of the contributions of AOs of each atom to the MOs suggests that for 2oxo compounds the most probable coordination sites are N5 and O4, whereas, for 2-thio compounds, these sites may be displaced by the S2 atom, because it contributes in more extent to the most available

| Compound | Binding energy (kcal mol <sup>-1</sup> ) |           | Heat of formation (kcal mol <sup>-1</sup> ) |         | Dipole moment<br>(Debyes) |             |  |
|----------|--|-----------|---|---------|---------------------------|-------------|--|
|          | AM1                                      | PM3       | AMI   | PM3     | AM1                       | <b>PM</b> 3 |  |
| AAU      | - 1621.96                                | - 1638.50 | - 54.67                                     | - 71.21 | 4.401                     | 3.692       |  |
| 1MAAU    | - 1890.63                                | - 1911.67 | - 48.24                                     | - 69.28 | 4.758                     | 4.081       |  |
| 3MAAU    | - 1890.33                                | - 1912.15 | - 47.94                                     | - 69.77 | 3.780                     | 3.041       |  |
| DAAU     | - 2158.79                                | - 2185.25 | - 41.31                                     | - 67.78 | 4.146                     | 3.596       |  |
| TAAU     | - 1573.62                                | - 1574.60 | 0.51  | - 0.67  | 4.845                     | 5.028       |  |
| TIMAAU   | - 1841.00                                | - 1847.16 | 8.23  | 2.06    | 5.271                     | 5.332       |  |
| T3MAAU   | - 1841.53                                | - 1847.68 | 7.70  | 1.54    | 4.081                     | 4.274       |  |
| TDAAU    | - 2108.33                                | - 2119.08 | 15.99                                       | 5.24    | 4.463                     | 4.611       |  |

Table 5 Binding energies, heats of formation and dipole moments

occupied  $\sigma$ -MO. Unfortunately, as it has been previously stated, there is not any bibliographic data about the structure and coordination modes of metal complexes with these uracil ligands which led to corroborate these assumptions and, consequently, they must await experimental verification. However, structural studies on metal complexes with related uracils could corroborate in any extent these conclusions [9–13,32–38].

# 4. Supplementary material

Lists of structure factors and detailed LCAOs for all MO calculations and tables with (i) anisotropic thermal parameters, (ii) atomic coordinated for H atoms, (iii) torsion angles, (iv) comparison of experimental and AM1 and PM3 modeled geometries for the title compounds, (v) least-squares planes for X-ray and modeled structures and deviations from them, (vi) sum of the squared coefficients for the valence orbitals of each atom in the LCAO corresponding to the fourteen highest energy occupied MOs for each studied compound, and (vii) net atomic charge densities for non-carbon and nonhydrogen atoms, are available from the authors on request.

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