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# Physical Chemistry

## Quantum-chemical study of supramolecular complexes $(DPyEt)_n(AgNO_3)_m$

***T. S. Zyubina,*★ *V. F. Razumov, S. B. Brichkin, and V. M. Anisimov***

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
*142432 Chernogolovka, Moscow Region, Russian Federation.*
*Fax: +7 (096) 576 4009. E-mail: zyubin@icp.ac.ru*

The electronic structures and energies of formation of supramolecular complexes of dipyridylethylene with $AgNO_3$ were calculated by the semiempirical AM1/d method, at the Hartree—Fock level, and by the density functional theory (B3LYP/6-31G*).

**Key words:** dipyridylethylene, supramolecular complexes, semiempirical quantum-chemical calculations, *ab initio* quantum-chemical calculations, electronic structure.

It is known that dipyridyl (DPy) derivatives can form supramolecular complexes with different metals.[1—4] In particular, DPy tends to form linear chain structures, *viz.*, polymeric coordination compounds characterized by a successive alternation of metal atoms and dipyridyl ligands. Such linear chains, in turn, tend to form sandwich structures through intermolecular interactions[2] giving rise to three-dimensional regular quasicrystalline aggregates. There is no detailed information on intermediate steps of the transformation from the ligand—ion complex into a regular three-dimensional polymeric structure. Data on stabilities and structures of intermediate aggregates giving rise to crystal lattices are also lacking.

Since experimental investigation of the initial steps of formation of these structures presents difficulties, quantum-chemical simulation of possible supramolecular complexes and calculations of the energies of their formation provide important information for the interpretation of experimental data and elucidation of the mechanisms of the processes in question.

In the present study, we performed quantum-chemical simulation for the complex of dipyridylethylene (DPyEt) with the silver(I) ion. This choice was governed the fact that DPyEt is a rather small ligand from the viewpoint of modern quantum-chemical programs and available computing facilities and also taking into account that there is as yet no unambiguous theoretical interpretation of abundant experimental data.

### Calculation procedure

Preliminary calculations were carried out with the use of the new semiempirical AM1/d method, which allows one to take into consideration the d orbitals of transition metals.[5] The energy characteristics were refined using the *ab initio* Hartree—Fock

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(HF) method and the density functional theory (B3LYP) with the 6-31G* basis set for the C, N, O, and H atoms and the LanL2DZ basis set involving the LanL2 pseudopotential for the Ag atom, which are available in the GAUSSIAN-94[6] and GAUSSIAN-98[7] program packages. For comparison, we performed calculations taking into account all electrons with the B88-PW91 functional and the DZVP basis set[8,9] using the DGAUSS program[10] integrated with the CAChe graphical user interface.[11]

The B88-PW91/DZVP method is characterized by a small computing time and low requirements on computing facilities. This enables one to study complexes, which could not be calculated at the B3LYP/LanL2DZ level. The AM1/d method (hereinafter, AM1), in turn, allows one to carry out calculations for rather large supramolecular complexes. For example, in the present study structures containing up to six DPyEt molecules and 13 silver (I) ions along with the $NO_3^-$ counterions (experimental studies were carried out with the use of the $AgNO_3$ salt as the source of silver ions) were calculated by the AM1 method.

## Results and Discussion

**Electronic structures and bond energies of supramolecular complexes.** The bond energy is used as a characteristic reflecting the stability of supramolecular complexes. This energy is equal to the difference between the total energies of the complex and its starting components:

$$\Delta E = E((\mathrm{DPyEt})_n(\mathrm{AgNO_3})_m) - n\,E(\mathrm{DPyEt}) - m\,E(\mathrm{AgNO_3}),$$

To compare different supramolecular complexes, it is sometimes useful to analyze the specific bond energy $\Delta E_{\mathrm{sp}} = \Delta E/m$, *i.e.*, the average energy of the ligand—cation bond per silver(I) ion.

In all the calculated structures, the DPyEt ligand occurs as the planar *trans* isomer (Fig. 1, *a*). The bond lengths calculated at the HF level of theory have the following values: C(1)—C(2), 1.33 Å; C(2)—C(3), 1.48 Å;

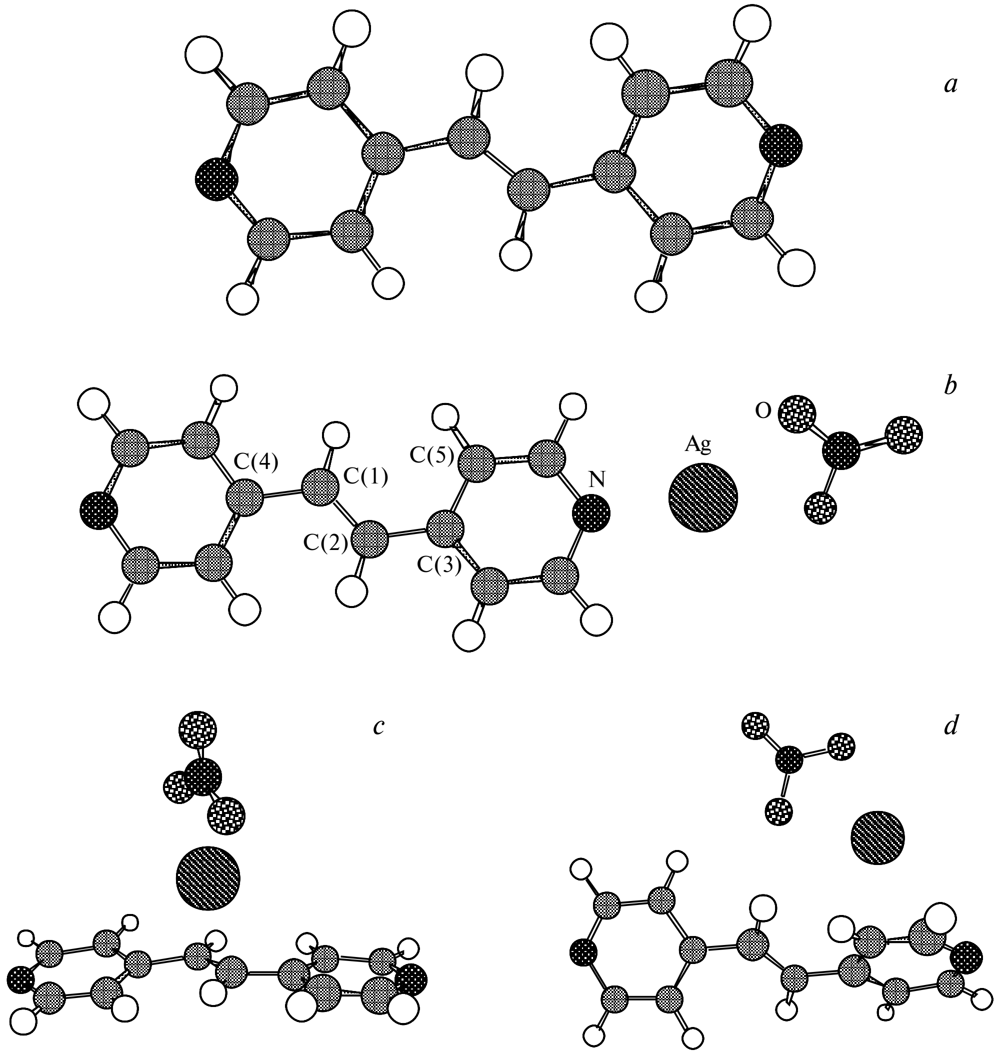

**Fig. 1.** Structures and bond types in the complexes DPyEt (*a*) and DPyEt·$AgNO_3$ (*b—d*): I (*b*), II (*c*), and III (*d*). The atomic numbering scheme corresponds to that presented in Fig. 1, *b*.

C(3)—C(5), 1.39 Å; C(5)—C(7), 1.39 Å; C(7)—N, 1.32 Å. The hypothetical $AgNO_3$ molecule also has a planar structure in which the Ag atom is bound to two O atoms. According to the results of calculations by the HF method, the corresponding bond lengths have the following values: Ag—O, 2.35 and 2.35 Å; N—O, 1.25, 1.25, and 1.18 Å.

The AOs of the N atoms, the central atoms (C(1) and C(2)), and the adjacent atoms of the pyridine ring make the major contribution to the HOMOs and LUMOs of dipyridylethylene. The HOMO and LUMO for the C(1)—C(2) bond are bonding and antibonding in character, respectively. Both these MOs belong to the orbitals of the π type. Two lower-lying quasidegenerate MOs (HOMO-1 and HOMO-2) are composed primarily of the AOs of the N atoms (these MOs belong to lone electron pairs of the N atoms). The quasidegenerate HOMO-3 and HOMO-4, which are orbitals of the π type and are composed of the AOs of the C atoms of the pyridine rings, have even lower energies. This orbital order was obtained in calculations by the B3LYP method. According to the results of calculations by the AM1 and HF methods, these two pairs of orbitals (HOMO-1, HOMO-2 and HOMO-3, HOMO-4) exchange places (are inverted), although they have very close energies. Analysis of the Mulliken populations showed that the negative charges on the individual atoms of the DPyEt molecule decrease in the series N > C(5) > C(1) (according to the results of HF calculations, −0.52, −0.28, and −0.19 *e*, respectively).

The silver(I) cation can form three types of complexes with DPyEt. The most stable complex (see Fig. 1, *b*) in which the silver ion is coordinated by the N atom is assigned to the first type. (Hereinafter, this type of complexes is denoted by I.) The second type of complexes (hereinafter, II) corresponds to the coordination of the silver ion at the central double bond of DPyEt (see Fig. 1, *c*). The third type of complexes (hereinafter, III) corresponds to the bonding of the silver cation with the aromatic π system of the pyridine ring (see Fig. 1, *d*).

The involvement of the silver ion into an interaction with the DPyEt molecule leads to the partial electron density transfer from DPyEt to $Ag^+$ and a decrease in the effective positive charge on the metal cation by 0.1—0.3 *e*, whereas the negative charge on the $NO_3$ anion and the positive charge on the DPyEt molecule are increased by 0.1—0.2 and 0.2—0.5 *e*, respectively. The appearance of the positive charge on the DPyEt molecule leads to a decrease in the energy of its MOs in the complex compared to that in the free state and causes changes in the energy gaps between the occupied and unoccupied MOs.

The principal geometric parameters of the $DPyEt \cdot AgNO_3$ complexes (of 1 : 1 composition) are given in Table 1. It can be seen that the C(1)—C(2) bond length calculated at the B3LYP/LanL2DZ level of theory is 0.02—0.04 Å larger and the X—Ag bond length is 0.15—0.35 Å smaller than those calculated by the HF/LanL2DZ method. The corresponding geometric parameters calculated by the B3LYP/LanL2DZ and B88-PW91/DZVP methods are identical within 0.01—0.03 Å and 2°. The C(1)—C(2) and X—Ag bond lengths calculated by the AM1 method are in better agreement with those calculated at the B3LYP/LanL2DZ level of theory than with those calculated at the HF/LanL2DZ level of theory.

The $NO_3^-$ counterion plays an important role in the complex formation. For example, as can be seen from Table 2, the bond energies in the $Ag^+$—DPyEt complexes (I and II) are 1.5—2 times higher that those in the

**Table 1.** Bond lengths and the C—X—Ag angle characterizing the $Ag^+$—DPyEt coordination bonds in the $Ag^+(DPyEt)$ and $Ag^+(DPyEt)NO_3^-$ complexes in which the $Ag^+$ atom is coordinated at the N, C(1), and C(5) atoms of the DPyEt molecule

| Parameter | $Ag^+(DPyEt)$ | | $Ag^+(DPyEt)NO_3^-$ | | | Method |
|---|---|---|---|---|---|---|
| | N | C(1) | N | C(1) | C(5) | |
| Bond length/Å | | | | | | |
| C(1)—C(2) | 1.35 | 1.37 | 1.34 | 1.37 | 1.34 | AM1 |
| | | | 1.33 | 1.34 | 1.33 | HF/LanL2DZ |
| | 1.35 | 1.39 | 1.35 | 1.38 | — | B3LYP/LanL2DZ |
| | | | 1.36 | 1.40 | 1.36 | B88-PW91/DZVP |
| X—Ag | 2.16 | 2.44 | 2.17 | 2.38 | 2.30 | AM1 |
| | | | 2.36 | 2.72 | 2.74 | HF/LanL2DZ |
| | 2.17 | 2.44 | 2.21 | 2.37 | — | B3LYP/LanL2DZ |
| | | | 2.24 | 2.34 | 2.39 | B88-PW91/DZVP |
| Angle | | | | | | |
| C—X—Ag/deg | 120 | 73.1 | 120 | 71.5 | 100.9 | AM1 |
| | | | 120 | 75.8 | 99.1 | HF/LanL2DZ |
| | 120 | 73.5 | 120 | 73.0 | | B3LYP/LanL2DZ |
| | | | 120 | 74.9 | 109.0 | B88-PW91/DZVP |

**Table 2.** Specific bond energies ($\Delta E_{sp}$)* in the $Ag^+$ complexes with DPyEt

| Structure | $-\Delta E_{sp}$/kJ $mol^{-1}$ | | Bond type | Method |
|---|---|---|---|---|
| | Without the counterion | With the $NO_3^-$ ion | | |
| $Ag^+$—DPyEt | 168.6 | 107.5 | I | AM1 |
| | | 89.9 | I | HF/LanL2DZ |
| | 235.1 | 130.9 | I | B3LYP/LanL2DZ |
| | | 108.3 | I | B88-PW91/DZVP |
| | 151.5 | 104.1 | II | AM1 |
| | | 37.2 | II | HF/LanL2DZ |
| | 147.7 | 85.3 | II | B3LYP/LanL2DZ |
| | | 71.9 | II | B88-PW91/DZVP |
| | | 96.2 | III | AM1 |
| | | 46.8 | III | HF/LanL2DZ |
| | | 58.1 | III | B88-PW91/DZVP |
| $Ag^+$—DPyEt—$Ag^+$ | 95.4 [22.6] | 103.3 [99.2] | 2 I | AM1 |
| | | 84.9 [79.5] | 2 I | HF/LanL2DZ |
| | 152.7 [69.9] | 125.9 [120.5] | 2 I | B3LYP/LanL2DZ |
| | | 102.9 [97.5] | 2 I | B88-PW91/DZVP |
| $Ag^+$—$(DPyEt)_2$ | 338.9 [170.3] | 133.0 [25.5] | 2 I | AM1 |
| | 434.7 [199.6] | 186.6 [55.6] | 2 I | B3LYP/LanL2DZ |
| | | 144.7 [36.4] | 2 I | B88-PW91/DZVP |

* Energies of bonding of the second unit in the chain are given in brackets.

$Ag^+$(DPyEt)—$NO_3^-$ complexes of the analogous types, and the differences between the corresponding energies for the $Ag^+$(DPyEt) complexes of types I and II are 2—4 times larger than those for the $Ag^+$(DPyEt)—$NO_3^-$ analogs. Compared to the results of AM1 calculations, the differences between the bond energies for complexes I and II without the counterion, which were calculated at the HF and B3LYP levels, are 10—40 kJ $mol^{-1}$ larger.

The presence of the $NO_3^-$ counterion is of even greater importance in the consideration of more complicated compounds. Actually, the bond energy in the $Ag^+$(DPyEt) complex is ~169—235 kJ $mol^{-1}$, whereas the energy of the bond between the $Ag^+$ cation and the N atom of another pyridine ring (Fig. 2, *a*) is substantially lower (23—70 kJ $mol^{-1}$). At the same time, the analogous energies of bonding of the $Ag^+$ cation in the presence of the $NO_3^-$ anion are virtually equal (103—126 and 99—121 kJ $mol^{-1}$, respectively). Apparently, the large difference in the energies of bonding of the first and second $Ag^+$ cations results from the Coulomb repulsion. Evidently, the energies of the bonds between both silver ions and the DPyEt molecules in the complex of 1 : 2 composition (see Fig. 2, *a*) must have close values. The bonding of the second silver ion leads to a somewhat weakening of the bond of the first bound ion.

For the complexes containing two DPyEt molecules and one $Ag^+$ cation, the energy of bonding of the second DPyEt molecule in the $Ag^+(DPyEt)_2$ complex is 4—7 times higher than that in the $Ag^+(DPyEt)_2NO_3^-$ complex. Therefore, the addition of DPyEt to the $Ag^+$(DPyEt) complex leads to the gain in energy of ~170—200 kJ $mol^{-1}$, whereas the analogous addition to $Ag^+(DPyEt)_2NO_3^-$ leads to the gain in energy of 25—55 kJ $mol^{-1}$. The typical bond energies published[1—4] for coordination polymers of this type are close to 40 kJ $mol^{-1}$. A comparison of the published data with the results of our calculations confirmed that it is important to take into account the counterion.

On the whole, the specific bond energies calculated by the AM1 method are consistent with those calculated at the B88-PW91/DZVP level of theory (within 2—38 kJ $mol^{-1}$) and with those calculated by the B3LYP method (within 20—30 kJ $mol^{-1}$). In addition, the same tendencies for changes in the corresponding energies are observed for analogous series in spite of substantial differences in the calculation procedures employed.

**Characteristic structural features of the complexes.** The complex with composition $Ag^+_2(DPyEt)(NO_3^-)_2$ ($n = 1$, $m = 2$) can be formed in three ways. The first mode of bonding involves the coordination of both $Ag^+$ ions to the N atoms (see Fig. 2, *a*), the Ag—N bond lengths varying from 2.16 Å (AM1) to 2.27 Å (DFT) depending on the calculation method. In the case of the second mode of complex formation, one $Ag^+$ ion is coordinated to the N atom, whereas the second $Ag^+$ ion is coordinated at the central C(1)—C(2) bond (see Fig. 2, *b*), the Ag—C(1) distances ranging from 2.36 (DFT) to 2.39 (AM1) Å, and the Ag—C(1)—C(2) angle is 73°. In the third case, one $Ag^+$ ion is coordinated to the N atom and another $Ag^+$ ion is coordinated at the π system of the pyridine ring (see Fig. 2, *c*), the Ag—C(5) distance is 2.30 Å (AM1), and the Ag—C(5)—C(3) angle is 101—109°. In the complexes of

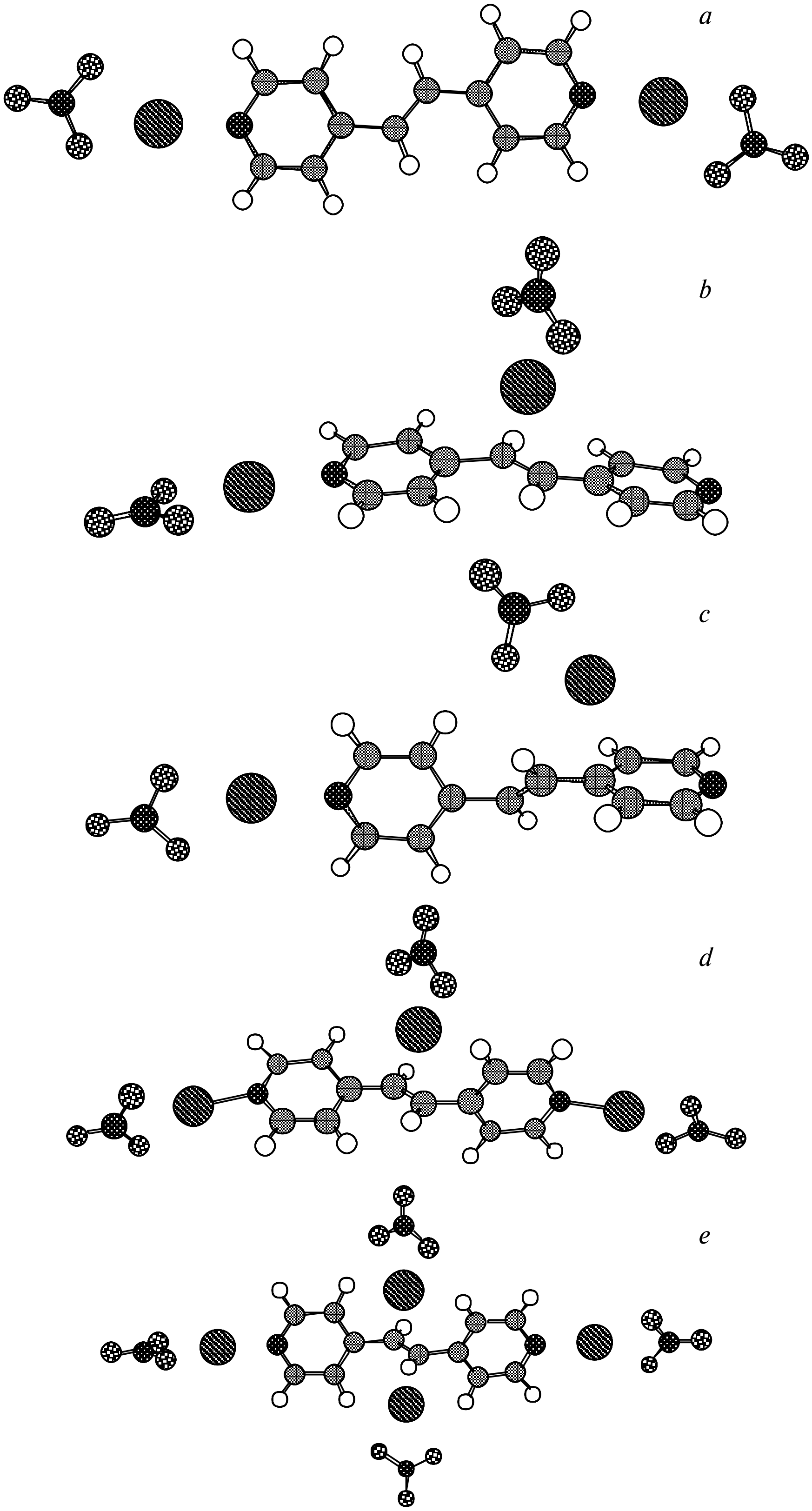

**Fig. 2.** Structures and bond types in the complexes (DPyEt)$(AgNO_3)_2$, 2 I (*a*); (DPyEt)$(AgNO_3)_2$, I, II (*b*); (DPyEt)$(AgNO_3)_2$, I, III (*c*), (DPyEt)$(AgNO_3)_3$, 2 I, II (*d*); and (DPyEt)$(AgNO_3)_4$, 2 I, 2 II (*e*). The numbers in front of the bond types indicate how many bonds of this type are present in the complex. The atomic numbering scheme corresponds to that presented in Fig. 1, *b*.

type I, the terminal Ag—N bond lengths are in the range of 2.16—2.17 Å, *i.e.*, these lengths are close to the values determined in X-ray diffraction studies of analogous complexes.[12,13]

The complex with the first mode of coordination (Table 3) in which both $Ag^+$ ions are bound to the N atoms is energetically most favorable (see Fig. 2, *a*). In the complex with the second mode of coordination, the bond energy (see Fig. 2, *b*) is 23 kJ mol$^{-1}$ lower (B3LYP) than that in the complex of the first type, and the bond energy for the complexes of the third type (see Fig. 2, *c*) is 7 kJ mol$^{-1}$ lower (AM1) than that for the complex with the second mode of coordination. Hence, the addition of the second $Ag^+$ cation together with the $NO_3^-$ anion to the $Ag^+(DPyEt)NO_3^-$ complex must occur predominantly at the N atom of the second pyridine ring. Let us denote this complex as $Ag^+{}_2(DPyEt)(NO_3^-)_2$-(I,I) (numbers in parentheses signify the bond types).

According to the results of AM1 calculations, the DPyEt molecule in the $Ag^+{}_2(DPyEt)(NO_3^-)_2$-(I,I) complex is twisted, *i.e.*, it adopts a propeller-like conformation due to rotation of the pyridine rings by 22°. An improvement in the accuracy of calculations leads to a decrease in this angle to 1—9°, but the barrier to rotation of the rings about the single bond remains low. This is attributable to the fact that the electron density is partially transferred (~0.5 *e*, AM1 method) from the DPyEt molecule to the $NO_3^-$ counterions and, consequently, the conjugation responsible for the planar structure of the isolated DPyEt molecule is weakened. Two more $Ag^+$

**Table 3.** Specific bond energies ($\Delta E_{sp}$) and dipole moments (*D*) of the $(Ag^+)_m(DPyEt)_n(NO_3^-)_m$ supramolecules (AM1 method)

| Supramolecule | *n* | *m* | Bond type | *D*/D | $\Delta E_{sp}$* /kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| **1** | 1 | 0 | — (see Fig. 1, *a*) | 0 | 0 |
| **2** | 1 | 1 | I (1) (see Fig. 1, *b*) | 12.7 | 107.5, (131.0), [108.4], {90.0} |
| **3** | 1 | 1 | II (1) (see Fig. 1, *c*) | 9.6 | 104.2, (85.4), [72.0], {37.2} |
| **4** | 1 | 1 | III (1) (see Fig. 1, *d*) | 9.5 | 96.2, [58.2], {46.9} |
| **5** | 1 | 2 | 2 I (2) (see Fig. 2, *a*) | 0 | 103.3, (125.9), [102.9], {84.9} |
| **6** | 1 | 2 | I (1), II (1) (see Fig. 2, *b*) | 14.8 | 101.7, (102.5) |
| **7** | 1 | 2 | I (1), III (1) (see Fig. 2, *c*) | 18.5 | 95.8 |
| **8** | 1 | 3 | 2 I (2), II (1) (see Fig. 2, *d*) | 5.1 | 95.0, [87.4] |
| **9** | 1 | 4 | 2 I (2), 2 II (2) (see Fig. 2, *e*) | 0 | 84.9 |
| **10** | 2 | 1 | 2 II | 8.2 | 154.8, (105.9), [80.3] |
| **11** | 2 | 1 | 2 I | 9.8 | 133.1, (186.6), [144.8] |
| **12** | 2 | 2 | 2 I (1), III | — | 121.7 |
| **13** | 2 | 2 | 3 I (1) | 14.1 | 119.2 |
| **14** | 2 | 2 | 2 I (2) | 11.2 | 117.1 |
| **15** | 2 | 2 | 4 I | 0 | 86.2 |
| **16** | 2 | 3 | 4 I (2) | 2.3 | 113.8 |
| **17** | 2 | 4 | 4 I, IVa, IVb (see Fig. 4) | 15.0 | 113.4 |
| **18** | 2 | 5 | 4 I (4), II, III | 16.5 | 108.8 |
| **19** | 2 | 5 | 4 I (2), 2 II (2) | 7.6 | 104.2 |
| **20** | 2 | 5 | 4 I (4), 2 II (see Fig. 5, *b*, *c*) | 10.3 | 102.1 |
| **21** | 2 | 6 | 4 I (4), II, III, IVa | 14.7 | 106.7 |
| **22** | 2 | 6 | 4 I (4), 2 II (2) | 10.9 | 102.9 |
| **23** | 2 | 6 | 3 I (1), 4 II (4) | 11.2 | 95.0 |
| **24** | 2 | 7 | 4 I (2), 3 II (2), 2 IVb | 23.1 | 112.1 |
| **25** | 2 | 7 | 4 I (3), 3 II (2), IVb | 4.1 | 110.9 |
| **26** | 2 | 7 | 4 I (2), 4 II (4) | 4.9 | 90.8 |
| **27** | 3 | 1 | 3 I | 9.5 | 141.0, [167.4] |
| **28** | 3 | 1 | 2 I, II | 9.4 | 138.5 |
| **29** | 3 | 4 | 5 I (2), III | 14.0 | 121.7 |
| **30** | 3 | 4 | 4 I (2), 2 III (see Fig. 3, *e*) | 25.2 | 120.9 |
| **30´** | 3 | 4 | 6 I (3) | 4.1 | 113.8 |
| **31** | 3 | 5 | 6 I (4), II | — | 121.7 |
| **32** | 4 | 1 | 4 I | 9.4 | 157.7 |
| **33** | 4 | 4 | 7 I (1), | 12.7 | 123.8 |
| **34** | 4 | 5 | 6 I (4), III, IVa | 13.1 | 135.1 |
| **35** | 4 | 5 | 7 I (1), II (1), | 7.2 | 127.6 |
| **36** | 4 | 5 | 4 I, 4 II (4) | 11.6 | 123.8 |
| **37** | 4 | 5 | 8 I (2) (see Fig. 3, *a*) | 2.3 | 121.3 |
| **38** | 4 | 5 | 8 I (4) (see Fig. 3, *b*) | 1.6 | 112.1 |
| **39** | 4 | 6 | 8 I (2), IVa | 21.9 | 132.6 |
| **40** | 4 | 6 | 8 I (4), II ((see Fig. 3, *d*) | 22.7 | 125.9 |
| **41** | 4 | 6 | 8 I (2), IVb | 25.9 | 125.5 |
| **42** | 4 | 7 | 8 I (4), 2 II (2) | 6.0 | 96.2 |
| **43** | 4 | 8 | 8 I (2), IVa, 2 IVb | 27.6 | 132.2 |
| **44** | 4 | 9 | 5 I (4), 4 II, 2 IVa (see Fig. 5, *a*) | 2.6 | 117.6 |
| **45** | 4 | 9 | 8 I (4), 4 II (4) | 10.7 | 108.8 |
| **46** | 4 | 11 | 8 I (4), 2 II (2) | 6.0 | 110.9 |
| **47** | 5 | 11 | 10 I (6), 5 II (3) | 6.8 | 114.6 |
| **48** | 6 | 11 | 12 I (8), 4 II | 10.5 | 116.7 |
| **49** | 6 | 13 | 12 I (8), 6 II (2) | 5.1 | 114.2 |

* Values calculated at the B3LYP/LanL2DZ, B88-PW91/DZVP, and HF/LanL2DZ levels of theory are given in parentheses, brackets, and braces, respectively.

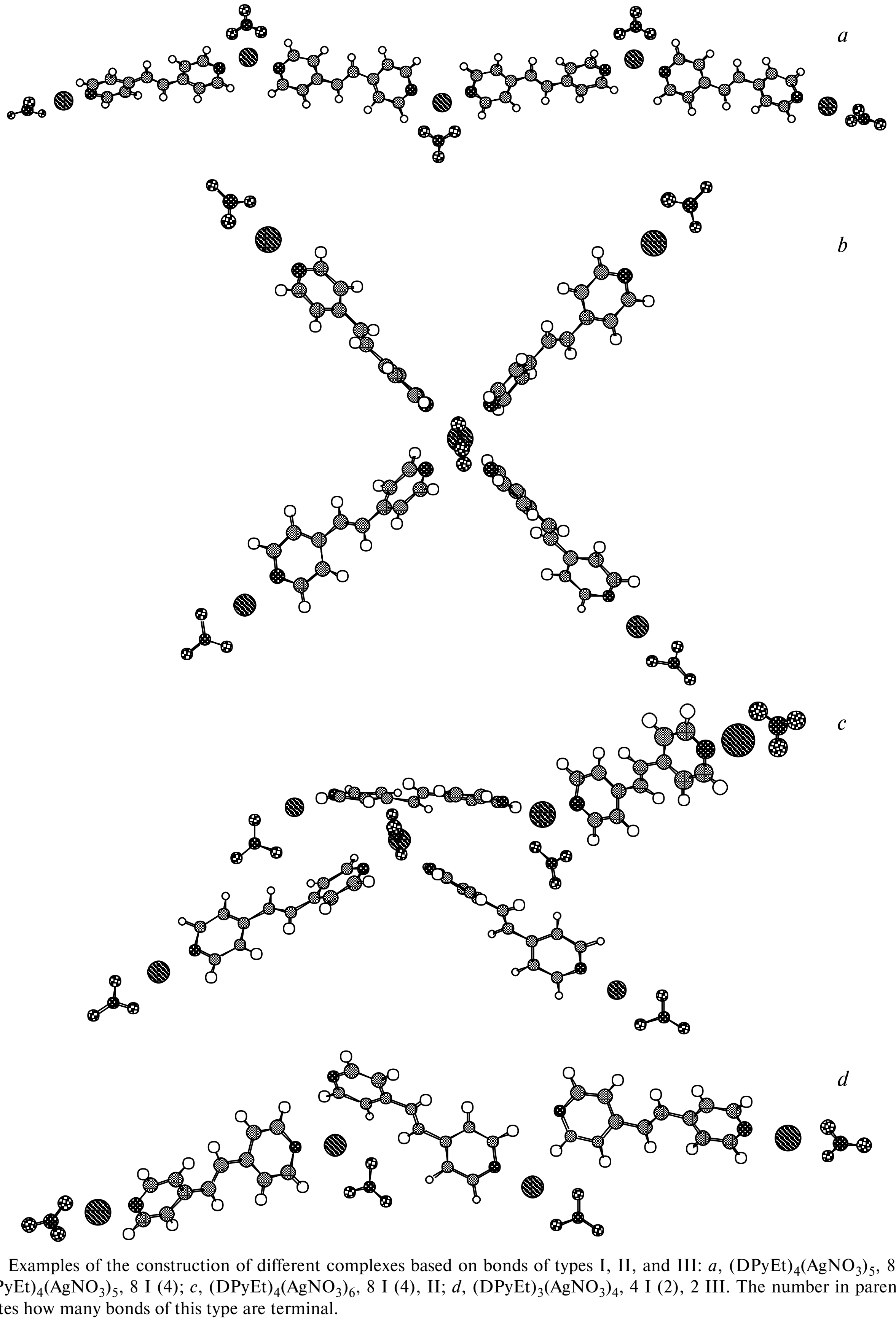

**Fig. 3.** Examples of the construction of different complexes based on bonds of types I, II, and III: *a*, $(\mathrm{DPyEt})_4(\mathrm{AgNO}_3)_5$, 8 I (2); *b*, $(\mathrm{DPyEt})_4(\mathrm{AgNO}_3)_5$, 8 I (4); *c*, $(\mathrm{DPyEt})_4(\mathrm{AgNO}_3)_6$, 8 I (4), II; *d*, $(\mathrm{DPyEt})_3(\mathrm{AgNO}_3)_4$, 4 I (2), 2 III. The number in parentheses indicates how many bonds of this type are terminal.

cations together with two $NO_3^-$ anions can be added to the $Ag^+{}_2(DPyEt)(NO_3^-)_2$-(I,I) complex at the central C(1)—C(2) bond (π system) on opposite sides (see Fig. 2, *d*, *e*).

The above-considered complexes provide the basis for the construction of more complicated supramolecular structures. In three types of complexes shown in Figs. 1 and 2, the typical distances from the Ag atom to the N atom involved in the $NO_3^-$ counterion are in the range of 2.74—2.76 Å. In these complex compounds, the positive charge on the $Ag^+$ ion is 0.22—0.23 *e* smaller than that in the free $AgNO_3$ molecule, and the negative charge on the $NO_3$ group is 0.05—0.12 *e* larger.

The more complicated supramolecular complexes $(DPyEt)_n(AgNO_3)_m$ can be constructed from the above-considered simple compounds involving different bond types (see Figs. 1 and 2). In the chain structures formed through bonds of the first type, the Ag—N bond lengths in the middle of the chain (internal N—Ag—N bonds) are in the range of 2.21—2.29 Å (AM1), *i.e.*, these bonds are 0.09—0.14 Å longer than the terminal bonds. Figure 3, *a* shows the structure of the chain supramolecular complex $Ag^+{}_5(DPyEt)_4(NO_3^-)_5$, which contains eight bonds of type I two of which are terminal. The planes of the pyridine rings of the adjacent ligands in the chain are rotated with respect to each other by 42.5° (B3LYP).

The centrosymmetrical supramolecular complex (star-like structure) with the overall composition $Ag^+{}_5(DPyEt)_4(NO_3^-)_5$, which is identical with that of the above-mentioned chain complex, has a radically different structure (see Fig. 3, *b*). This centrosymmetrical complex also contains eight bonds of type I, but four of these bonds are terminal, and one central $Ag^+$ cation is coordinated by four DPyEt molecules. In the latter complex, the internal Ag—N bond lengths of the central cation are increased to 2.37—2.41 Å (AM1) compared to those in the chain structure. These bond lengths differ by ~0.04—0.07 Å from those determined by X-ray diffraction analysis[14] of analogous structures with the $BF_4^-$ counterion and agree well with those found[15] for $[Ag(pyz)(BF_4)]$ (pyz is pyrazine). The distance from the $Ag^+$ cation to the N atom involved in the $NO_3^-$ anion increases from 2.74 to 2.89 Å (AM1) on going from chains to "stars".

The bond energies of different supramolecular complexes $(DPyEt)_n(AgNO_3)_m$ with $n$ = 1—6 and $m$ = 1—13 are given in Table 3.

Supramolecular complexes can be constructed by combining bonds of different types. The structure corresponding to the formula $Ag^+{}_6(DPyEt)_4(NO_3^-)_6$ (see Fig. 3, *c*) can be considered as that formed by two identical $Ag^+{}_3(DPyEt)_2(NO_3^-)_3$ chains, which are linked through a bond of type II. Hence, this supramolecular complex contains eight bonds of type I (four of which are terminal) and one bond of type II. As an example, yet another chain structure, *viz*., $Ag^+{}_4(DPyEt)_3(NO_3^-)_4$, is shown in Fig. 3, *d*. In this complex, bonds of types I and III alternate with each other.

In addition to the above-considered three types of bonds, the fourth type (IV) of bonds can occur. Bonds of this type correspond to interactions of the $Ag^+$ cation with two $NO_3^-$ anions, *i.e.*, the $Ag^+$ cation interacts not only with its own anion but also with the $NO_3^-$ anion of the adjacent $Ag^+$ cation. In these complexes, the Ag—Ag distances are in the range of 3.23—3.61 Å (AM1). It should be noted that the sum of the van der Waals radii of two Ag atoms is 3.40 Å. The distance from the $Ag^+$ cation to the adjacent N atoms of the $NO_3^-$ anions are 2.79 and 3.35 Å, respectively. The distances between the N atoms of the adjacent $NO_3^-$ ions are in the range of 4.60—4.73 Å (AM1). Let us denote this type of bonds by IVa. In this case, the $Ag^+$ ions are not involved in a direct bond and are linked to each other through the counterions, like in the $[Cu(C_2O_2H_3)_2H_2O]_2$ [16] and $[(3,4'\text{-bpy})(Br)Cu^I]_n$ systems.[17]

Another mode of bonding is also possible, such that the $Ag^+$ cations are coordinated by the ligands in different ways, *viz*., one cation is coordinated by two $NO_3^-$ anions (its own and adjacent), whereas another cation is coordinated only by its own anion. The Ag—Ag distances in such complexes are in the range of 3.87—4.87 Å. The distances from the first $Ag^+$ cation to the adjacent $NO_3^-$ anion are in the range of 3.24—3.37 Å. Let us denote this type of bonds by IVb. The involvement of bonds of type IV in the complex formation leads to a substantial expansion of the spectrum of possible configurations of supramolecules.

Figure 4 presents the supramolecular complex $Ag^+{}_4(DPyEt)_2(NO_3^-)_4$, in which bonds of types IVa and IVb are combined. This complex can be considered as a result of interaction of two $Ag^+{}_2(DPyEt)(NO_3^-)_2$ complexes (see Fig. 2, *a*), bonds of type IV being responsible for the virtually planar structures of both DPyEt molecules. In the supramolecular complex presented in Fig. 4,

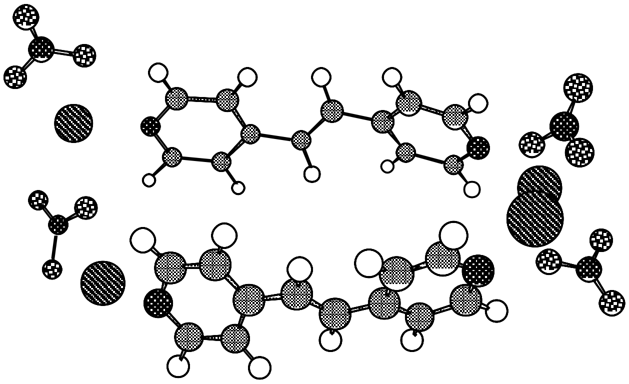

**Fig. 4.** Example of the formation of bonds of types IVa (right) and IVb (left) in the $(DPyEt)_2(AgNO_3)_4$ complex, 4 I, IVa, IVb.

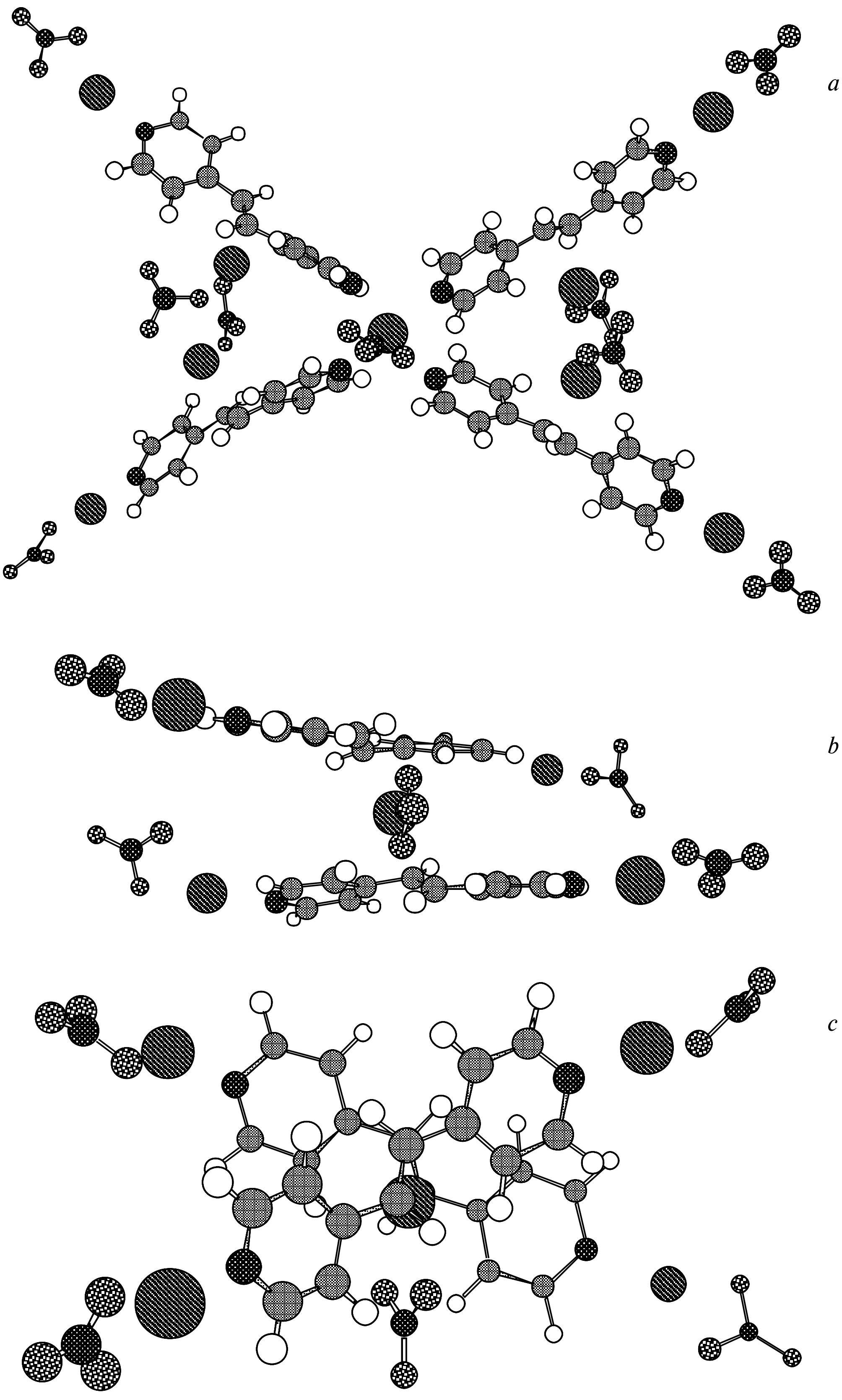

**Fig. 5.** Structures of the complexes $(DPyEt)_4(AgNO_3)_9$, 8 I (4); 4 II, 2 IVa (*a*); and $(DPyEt)_2(AgNO_3)_5$, 4 I (4), 2 II (side view (*b*) and top view (*c*)).

a bond of type IVa (Ag—Ag is 3.47 Å) and a bond of type IVb (Ag—Ag is 4.87 Å) are shown to the right and left, respectively. The distance between the central double bonds of the adjacent DPyEt molecules is 6.52 Å.

The $Ag^+{}_9(DPyEt)_4(NO_3{}^-)_9$ supramolecule, which is generated by the addition of four $Ag^+$ cations and $NO_3{}^-$ anions to $Ag^+{}_5(DPyEt)_4(NO_3{}^-)_5$ (see Fig. 3, *b*), is shown in Fig. 5, *a*. In this complex, the $Ag^+$ cations form bonds of type II with the adjacent DPyEt molecules and are linked in pairs through bonds of type IVa. This supramolecular complex $Ag^+{}_9(DPyEt)_4(NO_3{}^-)_9$ contains eight bonds of type I (four of which are terminal), four bonds of type II, and two bonds of type IVa.

Such complexes can interact with each other and with other supramolecules (for example, with complexes analogous to those presented in Figs. 2, *a* and 3, *b*) through the cleavage of bonds of type IVa and the formation of bonds of type II. These interactions can give rise to sandwich structures, like an interaction of $Ag^+{}_2(DPyEt)(NO_3{}^-)_2$ with $Ag^+{}_3(DPyEt)(NO_3{}^-)_3$ to form $Ag^+{}_5(DPyEt)_2(NO_3{}^-)_5$ (see Fig. 5, *b*, *c*). In this supramolecular complex, the distance between the double bonds of the DPyEt ligands is 4.79 Å, and the distances between the Ag atom and the C atoms involved in the double bonds are 2.50 Å. A possible mechanism of the construction of three-dimensional supramolecular crystal involves the two-dimensional as-

**Table 4.** Dissociation energies of selected supramolecular complexes[a] (Δ*E*, AM1 method)

| Supramolecules | Reaction | Bond type[b] | Δ*E*[c]/kJ mol$^{-1}$ |
|---|---|---|---|
| **13** → **2** + **2** | (DPyEt—M)$_2$ → (DPyEt—M) + (DPyEt—M) | I | 23.4 |
| **10** → **2** + **1** | M—(DPyEt)$_2$ → M—(DPyEt) + (DPyEt) | I | 25.5, (55.6), [36.4] |
| **13** → **5** + **1** | (DPyEt—M)$_2$ → (M—DPyEt—M) + (DPyEt) | I | 31.8 |
| **5** → **2** + M | (M—DPyEt—M) → (M—DPyEt) + M | I | 99.2 |
| **2** → M + **1** | (M—DPyEt) → M + (DPyEt) | I | 107.5, (131.0), [108.4] |
| **32** → **27** + **1** | M—(DPyEt)$_4$ → M—(DPyEt)$_3$ + (DPyEt) | I′ | 2.5 |
| **27** → **10** + **1** | M—(DPyEt)$_3$ → M—(DPyEt)$_2$ + (DPyEt) | I′ | 5.4, [22.6] |
| **38** → **16** + **2** (2) | M—(DPyEt—M)$_4$ → M—(DPyEt—M)$_2$ + 2 (DPyEt—M) | 2 I′ | 6.7 |
| **32** → **10** + **2** (1) | M—(DPyEt)$_4$ → M—(DPyEt)$_2$ + 2 (DPyEt) | 2 I′ | 6.7 |
| **38** → **30′** + **2** | M—(DPyEt—M)$_4$ → M—(DPyEt—M)$_3$ + (DPyEt—M) | I′ | 25.5 |
| **30′** → **16** + **2** | M—(DPyEt—M)$_3$ → M—(DPyEt—M)$_2$ + (DPyEt—M) | I′ | 34.3 |
| **49** → **47** + **5** | (M—DPyEt—M)(M—(DPyEt—2M)$_4$)(M—DPyEt—M) → → (M—DPyEt—M)(M—(DPyEt—2M)$_4$) + (M—DPyEt—M) | II | 16.3 |
| **20** → **8** + **5** | (M—DPyEt—M)—M—(M—DPyEt—M) → → (M—DPyEt—2M) + (M—DPyEt—M) | II | 18.8 |
| **11** → **2** + **1** | (DPyEt)—M—(DPyEt) → M—(DPyEt) + (DPyEt) | II | 50.6, (20.5), [8.4] |
| **20** → **5** + **8** | (M—DPyEt—M)(M—DPyEt—2M) → → (M—DPyEt—M) + (M—DPyEt—2M) | II | 52.7 |
| **9** → **8** + M | (2M—DPyEt—2M) → (M—DPyEt—2M) + M | II | 55.6 |
| **31** → **16** + **5** | (M—(DPyEt—M)$_2$)(M—DPyEt—M) → → (M—(DPyEt—M)$_2$) + (M—DPyEt—M) | II | 61.5 |
| **47** → **45** + **5** | (M—(DPyEt—2M)$_4$)(M—DPyEt—M) → → (M—(DPyEt—2M)$_4$) + (M—DPyEt—M) | II | 75.3 |
| **8** → **5** + M | (M—DPyEt—2M) → (M—DPyEt—M) + M | II | 78.2, [56.1] |
| **49** → **45** + **2** (5) | (M—DPyEt—M)(M—(DPyEt—2M)$_4$)(M—DPyEt—M) → → (M—(DPyEt—2M)$_4$) + 2 (M—DPyEt—M) | 2 II | 91.6 |
| **48** → **42** + **2** (5) | (M—DPyEt—M)(M—(DPyEt—2M)$_2$(DPyEt—M)$_2$)(M—DPyEt—M) → → (M—(DPyEt—2M)$_2$(DPyEt—M)$_2$) + 2 (M—DPyEt—M) | 2 II | 96.2 |
| **3** → M + **1** | (M—DPyEt) → M + (DPyEt) | II | 104.2, (85.4), [72.0] |
| **48** → **45** + **2** (8) | (M—DPyEt—M)(M—(DPyEt—2M)$_2$(DPyEt—M)$_2$)(M—DPyEt—M) → → (M—(DPyEt—M)$_4$) + 2 (DPyEt—3M) | 2 II | 153.1 |
| **30** → **16** + **2** | M—(DPyEt—M)$_3$ → M—DPyEt—M + 2 (DPyEt—M) | 2 III | 70.7 |
| **4** → M + **1** | (M—DPyEt) → M + (DPyEt) | III | 96.2, [58.2] |
| **39** → **16** + **16** | (M—(DPyEt—M)$_2$)$_2$ → M—(DPyEt—M)$_2$ + M—(DPyEt—M)$_2$ | IVa | 111.7 |
| **43** → **4** (5) | (M—DPyEt—M)$_4$ → 4 (M—DPyEt—M) | IVa, 2 IVb | 231.8 |

[a] For notations of the supramolecules, see Table 3, M ≡ $AgNO_3$.

[b] Numbers and types of the broken bonds are given; the "star"-type bonds are primed.

[c] Values calculated at the B3LYP/LanL2DZ and B88-PW91/DZVP levels of theory are given in parentheses and brackets, respectively.

sociation of star-like complexes through bonds of type I followed by their aggregation through bonds of type II. As can be seen from Table 3, most of supramolecular complexes have rather large dipole moments, which can facilitate their association.

**Dissociation energies of supramolecular complexes.** The calculated energies of dissociation of the above-considered supramolecular complexes into different components are given in Table 4. Most of the data were obtained by the AM1 method. For small complexes, the results of more precise calculations are also presented. Generally, the cleavage energies of bonds of type I calculated by the AM1 method are 25—29 and 4—8 kJ mol$^{-1}$ lower than those calculated at the B3LYP and B88-PW91 levels of theory, respectively. The cleavage energies of bonds of type II calculated by the AM1 method are 17—25 and 21-42 kJ mol$^{-1}$ higher than those calculated at the B3LYP and B88-PW91 levels of theory, respectively. The cleavage energy of bonds of type III calculated by the AM1 method is 38 kJ mol$^{-1}$ higher than that calculated by the B88-PW91 method.

As can be seen from Table 4, the energy required for the abstraction of the $Ag^+$ cation together with its counterion from the $DPyEt \cdot AgNO_3$ or $(DPyEt)(AgNO_3)_2$ compounds is 67—75 kJ mol$^{-1}$ higher than that required for the abstraction of DPyEt from the $Ag^+(DPyEt)_2NO_3^-$ or $Ag^+{}_2(DPyEt)_2(NO_3^-)_2$ chains. It should be noted that this result was obtained at all levels of theory. The energies of abstraction of DPyEt from the "stars" (bonds of type I′) are 17—25 kJ mol$^{-1}$ lower than those for the chain structures.

For structures with bonds of type II, the energy of abstraction of the $Ag^+$ cation together with the $NO_3^-$ anion from $Ag^+(DPyEt)NO_3^-$ is 48 kJ mol$^{-1}$ higher than that required for the analogous abstraction from $Ag^+{}_4(DPyEt)(NO_3^-)_4$ or for the abstraction of DPyEt from $Ag^+(DPyEt)_2NO_3^-$. The energies of abstraction of the $Ag^+{}_2(DPyEt)(NO_3^-)_2$ fragments from large ordered complexes having structures of associated "stars" are 25—54 kJ mol$^{-1}$ higher than those required for the abstraction from small (like $Ag^+{}_5(DPyEt)_2(NO_3^-)_5$) or disordered complexes.

For complexes with bonds of type III, the energy of abstraction of $Ag^+NO_3^-$ from $Ag^+(DPyEt)NO_3^-$ is 25 kJ mol$^{-1}$ higher than the energy of abstraction of two $Ag^+(DPyEt)NO_3^-$ complexes from the $Ag^+{}_4(DPyEt)_3(NO_3^-)_4$ chain. The energies of abstraction of $Ag^+{}_2(DPyEt)(NO_3^-)_2$ from complexes with bonds of type IV are 13—33 kJ mol$^{-1}$ (AM1) higher than the cleavage energies of bonds of type III and are somewhat lower than the cleavage energies of the corresponding bonds of type II.

The bond energies calculated for a large series of supramolecular complexes of dipyridylethylene with silver cations can serve as the basis for analysis of the corresponding experimental results[18].

The calculations were carried out on an RM600 supercomputer in the Computer Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences and on a Power Challenger L supercomputer in the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences (Russian Foundation for Basic Research, Project No. 98-07-90290).

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