

## Model considerations on physico-chemical nature of protein-nucleic acid contacts through amino acid carboxylic groups: spectroscopic data

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*This paper generalizes the results of a series of the works on spectroscopic (IR, UV, NMR, Raman) investigations of complexes of nucleotide bases, their numerous methyl and glycosyl derivatives with amino acid carboxylic groups modelling point protein-nucleic acid contacts. The specificity of interactions between bases and two forms of carboxylic group — neutral and deprotonated — was determined. The structures of the complexes investigated were established, and the role of various atomic groups in their formation was elucidated as well. Special consideration has been given to the frequent occurrence of proton transfer in the studied complexes. The significance of the data obtained in understanding of elementary mechanisms of protein-nucleic acid interactions is discussed.*

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Although the number of investigations on structures of protein-nucleic acid complexes by X-ray [1–6] and NMR spectroscopy [4–9] is continuously increasing, not in every case it is possible to distinguish unambiguously the fine architecture of point protein-nucleic acid contacts. Therefore, the study on elementary mechanisms of protein-nucleic acid recognition in more simple model systems [10–22] remains actual.

In the present brief survey we try to generalize the main physico-chemical features of interactions in the complexes modelling recognition of nucleotide bases, their nucleosides and a variety of their methyl derivatives by carboxylic groups of Asp and Glu in DMSO. The use of DMSO as a solvent allows us to observe rather strong interactions which exceed its interactions with the bases and amino acid carboxylic groups. The systematic studies of these complexes were conducted by means of UV, IR and NMR spectroscopies over the last few years [23–31]. Interpretations of the results were supported by the model semiempirical quantum-mechanical calculations [32].

Among non-substituted nucleotide bases and nucleosides only Cyt, weakly interacting with deprotonated carboxylic group (carboxylate-ion), was shown to form the strong complex with neutral carboxylic group through two H-bonds involving N3 atom and amino group or NH and C=O groups (according to the AM1 calculations [32] the latter scheme is prevailing) (Fig. 1). The results of IR and Raman investigations of solid state complexes of cytosine and amino acid carboxylic groups [23, 28], as well as <sup>13</sup>C NMR study in DMSO [25] evidence the proton transfer from carboxylic group to the base along the OH...N3 bond. Moreover, it was shown that in the triple complex f-Asp:Cyt:m<sup>9</sup>Gua amino acid carboxylic group, binding to Cyt, loosens H-bonds inside the base pair.

Quite the contrary, the other bases and nucleosides form specific complexes with carboxylate-ion, their interactions with neutral carboxylic group were not observed. Nevertheless, such interactions may be realized in less polar environment [33] in which the solvation of the ligands is lower.

It was demonstrated that imino and amino groups of the bases have a dominant role in formation of their complexes with carboxylate-ion. The mono-methylation of Gua and Ade amino groups doesn't

change the character of interaction with carboxylate-ion, increasing it considerably. To the point, the significant role of inversion and anisotropic rotation of the nucleotide bases' amino groups in DNA structure and functioning is discussed in the papers [34--38].

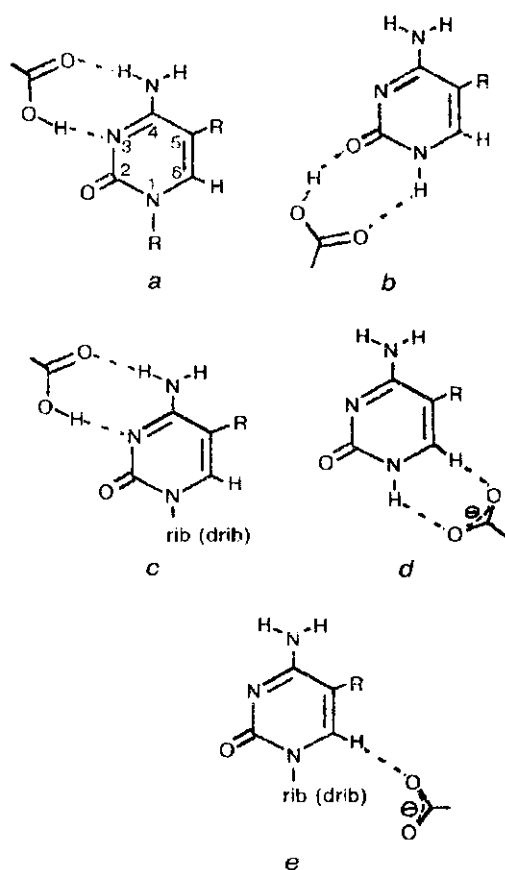


Fig. 1. Schemes of the complexes of: cytosine, 1-methylcytosine, 5-methylcytosine, 1,5-dimethylcytosine (a, b), cytidine, deoxycytidine, 5-methyldeoxycytidine (c) with neutral carboxylic group; cytosine, 5-methylcytosine (d), cytidine, deoxycytidine, 5-methyldeoxycytidine (e) with carboxylate-ion. Hereinafter abbreviations are  $R = H, CH_3$ ; rib(drib) = ribose(deoxyribose)

Carboxylate-ion forms highly specific complex with  $m^9$ Gua and G through two H-bonds involving the N1H imino and N2H amino groups, Ade — N6H amino and N7H imino groups [39] (the N9H  $\rightarrow$  N7H tautomeric transition of Ade complexed with carboxylate-ion was borne out by the quantum-chemical calculations [32]), Hyp — N1H and/or N9H imino groups, I — N1H imino group, X and  $m^9$ Xan — N3H imino groups, Xan — N3H and N9H imino groups,  $m^3$ Xan — N9H imino group (the N7H  $\rightarrow$  N9H tautomeric transition of Xan and  $m^3$ Xan complexed with carboxylate-ion was confirmed by quantum-chemical simulations [32]), Ura and Thy — N1H and/or N3H imino groups, U and T — N3H imino groups (Fig. 2). The determining role of bases' imino group as proton donor under H-bonded complex formation with carboxylate-ion is demonstrated by complete suppression of interactions with methylated at imino groups  $m^1$ G,  $m^1$ I,  $m_2^{1,3}$ Ura,  $m_2^{1,7}$ Gua,  $m^9$ Ade, as well as by noticeable weakening the interaction of  $m^1$ Cyt with carboxylic group and  $m^1$ Ura,  $m^3$ Ura,  $m^1$ Thy with carboxylate-ion.

The methylation of pyrimidine bases at the C5 position does not change the schemes of interactions in the complexes formed, the stability of the complexes of  $m^5$ Cyt and  $m_2^{1,5}$ Cyt with carboxylic group being significantly increased as compared to Cyt and  $m^1$ Cyt [27].

In general, almost all substitutions of the bases which don't involve the essential distortions of their rings retain specificity as to binding with neutral and deprotonated carboxylic group. To the contrary, methylations of the bases which change cardinaly the ring structure (the N1 and N3 positions of Ade, N3 — Gua, N3 — Cyt, N7 — purine nucleosides) cause alterations of types of the complexes formed (Fig. 3) and, as a rule, the reversion of the specific interactions with two forms of carboxylic group.

It might be well to point out the involvement of the C8H protons of  $m^7$ I,  $m^7$ X, and the C6H protons of pyrimidine bases in weak H-bonding with carboxylate-ion [30].

Carboxylate-ion was shown to interact with the O2'H, O3'H and O5'H glycosylic hydroxyls of nucleosides [40]. In the case of ribosides it forms two cooperative H-bonds with O2'H and O3'H groups. It should be noted that ribose (deoxyribose) and the base of nucleosides affect mutually their interactions with carboxylate-ion.

The obtained set of physico-chemical features of point protein-nucleic acid contacts is consistent with X-ray and NMR data concerning detailed architecture of nucleic acids complexes with various enzymes, regulatory proteins and drugs of peptidic nature and

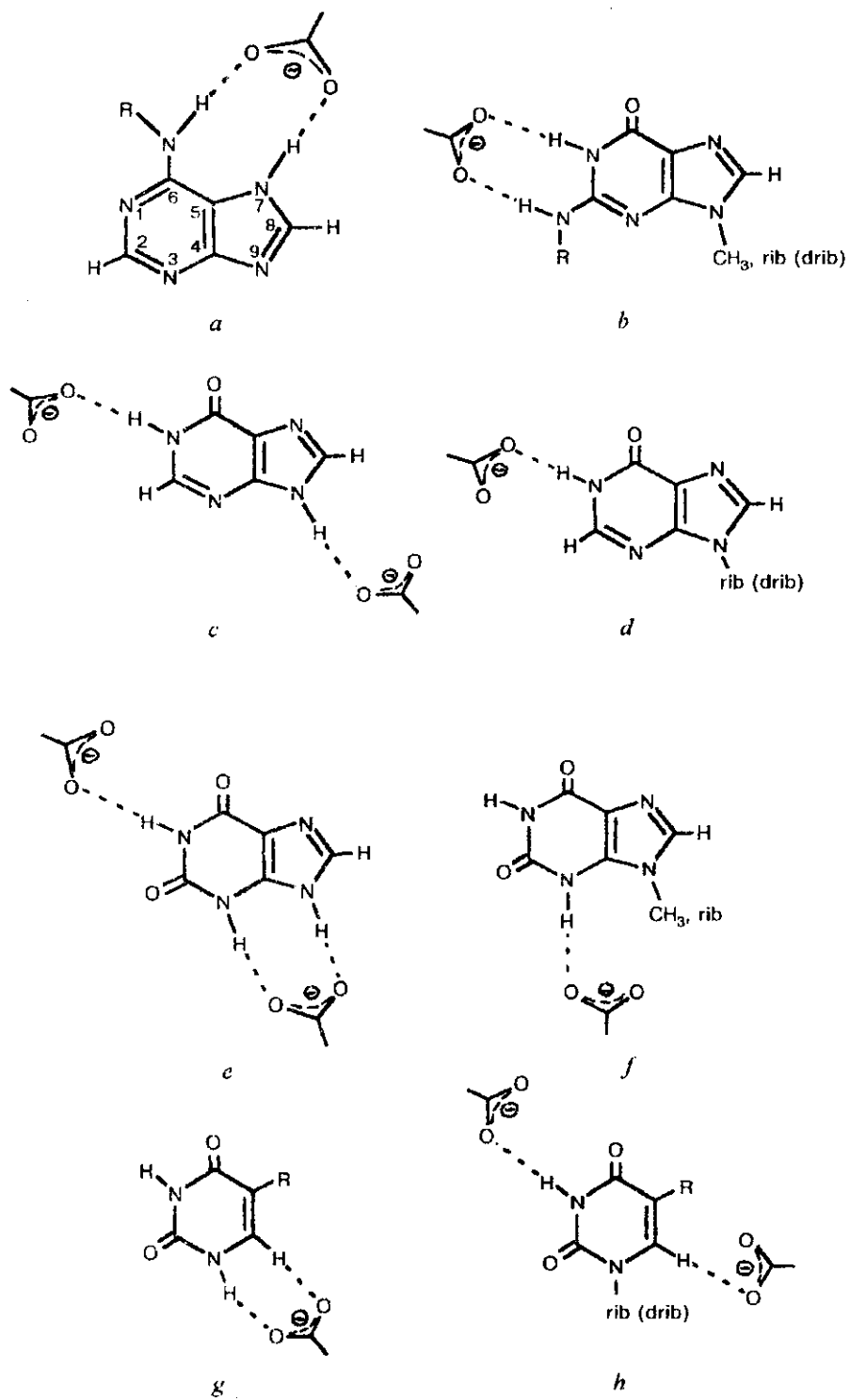


Fig. 2. Schems of the complexes of: adenine, 6-methyladenine (*a*), 9-methylguanine, 2,9-dimethylguanine, guanosine, deoxyguanosine, 2-methylguanosine (*d*), hypoxanthine (*c*), inosine, deoxyinosine (*d*), xanthine (*e*), 9-methylxanthine, xanthosine (*f*), uracil, thymine (*g*), uridine, deoxyuridine, thymidine, ribothymidine (*h*) with carboxylate-ion

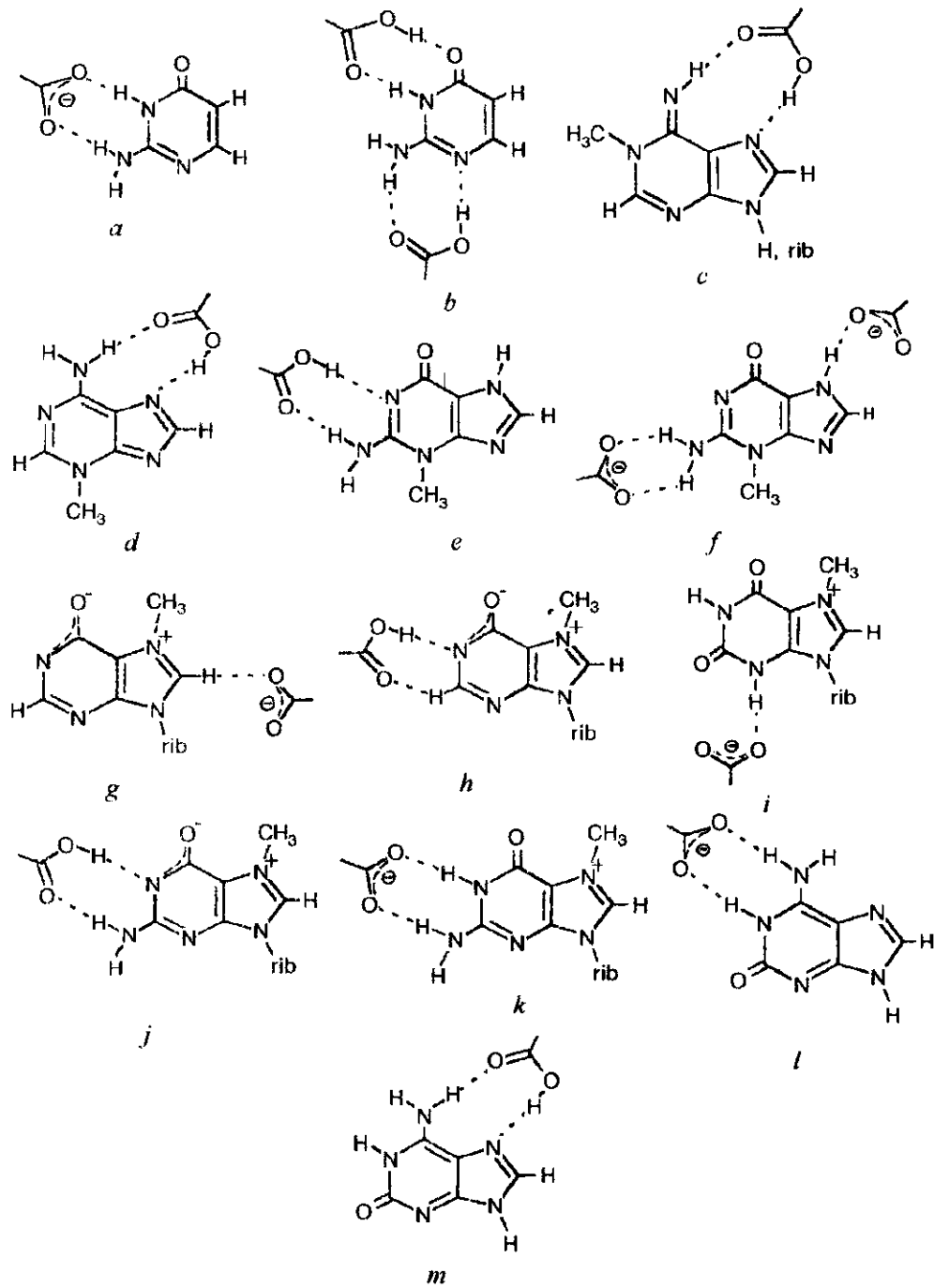


Fig. 3. Schemes of the complexes of: isocytosine (a), 3-methylguanine (f), 7-methylinosine (g), 7-methylxanthosine (i), 7-methylguanine (k), isoguanine (l) with carboxylate-ion; isocytosine (b), 1-methyladenine, 1-methyladenosine (c), 3-methyladenine (d), 3-methylguanine (e), 7-methylguanine (f), 7-methylinosine (h), 7-methylxanthosine (i), isoguanine (m) with neutral carboxylic group

could be applied to refinement of their structures and functioning. These data may be of use for design of biologically active substances of peptidic or nucleotide nature with aimed actions and understanding their therapeutic effects. There is the information on the participation of neutral and deprotonated forms of carboxylic group of Asp and Glu in formation of real protein-nucleic acid complexes. To cite examples, the complexes of 3- and 7-alkyl purine bases with repair enzymes [41, 42], glutamyl-tRNA synthetase with tRNA<sup>Gln</sup> [43, 44], seryl-tRNA synthetase with tRNA<sup>Ser</sup> [45, 46], ribonuclease T<sub>1</sub> with 2'-GMP [47], RNA with the coat protein in TMV [48], DNA with the glucocorticoid receptor [49], HhaI DNA cytosine-5-methyltransferase with its target cytosine and cofactor [50], mutation of Asn → Asp in thymidylate synthase converting the enzyme to a deoxycytidylate methylase [51], and others.

The most prominent feature of the complexes studied is a very common occurrence of proton transfer [31]. The protonation of bases on account of carboxylic group has been proved for Cyt, m<sup>5</sup>Cyt, m<sup>1</sup>Ade, m<sup>3</sup>Ade, m<sup>1</sup>A, m<sup>7</sup>G (A form) and m<sup>7</sup>I. The proton transfer from bases to carboxylate-ion was observed in the complexes of m<sup>3</sup>Cyt, m<sup>3</sup>Gua, m<sup>7</sup>G (B form), Hyp, Xan, m<sup>9</sup>Xan and X with deprotonated carboxylic group. There are some indications that Ura, Thy, isoGua, isoCyt are deprotonated in the complexes with carboxylate-ion.

Up-to-date physico-chemical biology attaches a great importance to proton transfer processes [52—54], which determine dynamic aspects of interactions between biopolymers, especially in nucleoprotein complexes.

It might be worth pointing that proton transfer processes determined by two well structure of the H-bond potentials are substantially nonlinear and environmental dependent. The proton polarizability of such H-bonds (ability of shifting along the H-bonds) may exceed electron polarizability by two orders [55] and increases while chains of H-bonds are formed because of collective motion of protons [56]. There is an idea, that chains of H-bonds with such potentials in real biopolymers and their complexes may be one of the causative factors of their non-linear dynamics and the possible routes for the signals of long-range control of biochemical reactions. It is the complexes investigated that give an impetus to conformational transitions and biochemical transformations at long distances.

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Фізико-хімічна природа модельних білково-нуклеїнових контактів через карбоксильну групу амінокислот: спектроскопічні дані

Резюме

Узагальнено результати серії робіт спектроскопічного (ІЧ, УФ, ЯМР, Раман) дослідження комплексів нуклеотидних основ та їхніх численних метил- та глікозилпрохідних з карбоксильною групою амінокислот, що моделюють точкові білково-нуклеїнові контакти. Встановлено специфічність взаємодії основ з двома формами карбоксильної групи — нейтральною та депротонованою. Визначено структуру досліджуваних комплексів, а також з'ясовано роль різних атомних груп основ у їхньому формуванні. Особливу увагу привертас поширеність явища перенесення протона в досліджених комплексах. Обговорюється значення отриманих результатів для розуміння елементарних механізмів білково-нуклеїнових взаємодій.

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Физико-химическая природа модельных белково-нуклеиновых контактов через карбоксильную группу аминокислот: спектроскопические данные

Резюме

Обобщены результаты серии спектроскопического (ИК, УФ, ЯМР, Раман) исследования комплексов нуклеотидных оснований и их многочисленных метил- и гликозилпроизводных с карбоксильной группой аминокислот, моделирующих точечные белково-нуклеиновые контакты. Установлена специфичность взаимодействия оснований с двумя формами карбоксильной группы. Определена структура исследованных комплексов, а также выяснена роль разных атомных групп оснований в их образовании. Особое внимание обращает на себя распространенность явления переноса протона в исследованных комплексах. Обсуждается значение полученных результатов для понимания элементарных механизмов белково-нуклеиновых взаимодействий.

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