Physical Chemistry

Electronic and spatial structures of some derivatives of 5-phosphoranylidenbarbituric and 5-phosphoranylidenthiobarbituric acids

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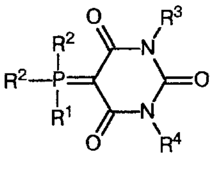
The spatial and electronic structures of some derivatives of 5-phosphoranylidenbarbituric and 5-phosphoranylidenthiobarbituric acids are investigated within the framework of the semiempirical MNDO approximation. The effect of the substituents at the phosphorus and nitrogen atoms on the geometry and distribution of electron density in the studied molecules is considered. Their pseudoaromatic π-system, which is formed by diffuse lone electron pairs of the $>\bar{C}-$ ion and two N atoms, involves alternating donor and acceptor centers. The pseudoaromatic fragment in these molecules is nearly planar, and the deviations from planarity are dependent on the size of the substituents at the phosphorus and nitrogen atoms.

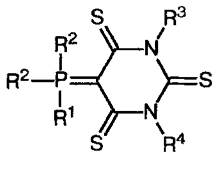
Key words: barbiturates, thiobarbiturates, spatial and electronic structures, semiempirical calculations.

Derivatives of barbituric acid can be involved in the formation of ordered hypermolecular structures with other nitrogen bases of the pyrimidine series via hydrogen bonds.[1] One may expect that crystalline structures composed of such units[1,2] will have new specific properties (optical, electric, and magnetic). The presence of hydrogen bonds between the "molecular units" restricts their possible orientations in the crystal and, therefore, enables one to carry out a directed search for hypermolecular structures with specific architecture and properties.[2] The necessary condition for the formation of crystal structures with hydrogen bonds is the planarity of the original heterocycles that may be affected by the introduction of any substituents.

This work concerns the geometric and electronic structures of some derivatives of 5-phosphoranyliden-



1a—h



2a—e

a: $R^1 = R^2 = R^3 = R^4 = H$;
b: $R^1 = Me$, $R^2 = R^3 = R^4 = H$;
c: $R^1 = R^3 = R^4 = H$, $R^2 = Me$
d: $R^1 = R^2 = Me$, $R^3 = R^4 = H$;
e: $R^1 = R^2 = Et$, $R^3 = R^4 = H$;
f: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$;
g: $R^1 = R^2 = R^3 = H$, $R^4 = Bu^t$;
h: $R^1 = R^2 = R^3 = H$, $R^4 = OH$

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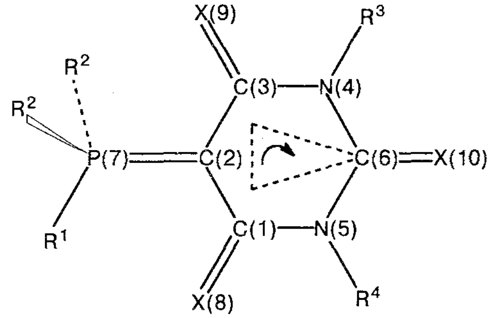
barbituric (**1**) and 5-phosphoranylidenthiobarbituric (**2**) acids, particularly, the effect of substituents at the phosphorus and nitrogen atoms on the geometric parameters and distribution of electron density in these molecules.

Experimental

The plane of the cycle is assumed to be the plane going through the carbon atoms of the carbonyl (or thiocarbonyl) groups, *i.e.*, the C(1), C(3), and C(6) atoms. The direction of rotation, which is used for determination of the angles of deviation of different atoms from the plane of the cycle, is assumed to be clockwise:



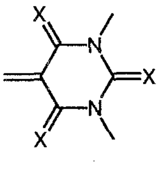
The angle of deviation of the C(2) atom from the plane of the cycle (α_2) is the minimum dihedral angle between the C(1)—C(2)—C(3) and C(1)—C(3)—C(6) planes, it is taken as positive, if the movement coincides with a right-hand screw rotated in the direction of rotation; otherwise it is negative. Similarly, we denote the α_4, α_5, α_8, α_9, and α_{10} angles, which characterize the deviations of the N(4) and N(5) atoms and the X(8), X(9), and X(10) substituents, respectively, from the plane of the cycle.

The degree of pyramidicity of bonds at the N(4) and N(5) atoms characterizes the angles of deviation of R^3 and R^4 from the N(4)—C(6)—C(3) and N(5)—C(1)—C(6) planes, respectively. These angles are denoted as β_4 and β_5, and their signs are assumed as in the case of the α_2, α_4, and α_5 angles.

The calculations were performed within the framework of MNDO approximation by using the MOPAC program with the complete optimization of all geometric parameters.

Results and Discussion

The main geometric parameters of the **1a—1d** and **2a—2d** molecules are represented in Tables 1 and 2. Using these data, we can conclude that in all molecules under consideration the fragment



has a nearly planar configuration: the angles of deviation of the atoms from the plane of cycle are within 6°; these distortions can be neglected in the qualitative description of the structure. This conclusion is rather common for the pyrimidine derivatives: the planar configuration of heterocycle is proved for many of them by both the experiments and calculations.[3,4]

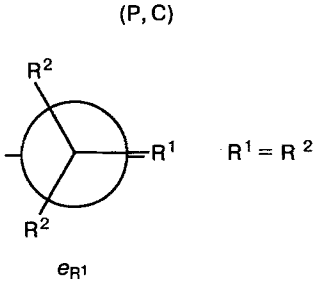
Table 1. Main geometric parameters of molecules **1a—1d**

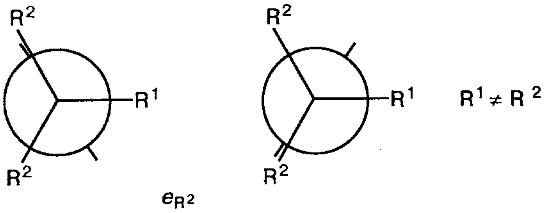
Parameter*	Molecule			
	1a	**1b**	**1c**	**1d**
C(1)—C(2)	1.447	1.445	1.446	1.446
C(2)—C(3)	1.448	1.446	1.446	1.449
C(3)—N(4)	1.421	1.422	1.423	1.424
C(1)—N(5)	1.421	1.421	1.424	1.426
N(4)—C(6)	1.407	1.406	1.405	1.403
N(5)—C(6)	1.406	1.405	1.404	1.402
C(2)—P(7)	1.680	1.690	1.703	1.721
C(1)=O(8)	1.236	1.236	1.237	1.237
C(3)=O(9)	1.236	1.237	1.237	1.238
C(6)=O(10)	1.230	1.230	1.230	1.231
C(1)—C(2)—C(3)	122.5	122.2	121.9	120.9
C(2)—C(3)—N(4)	115.6	115.9	116.2	116.6
C(2)—C(1)—N(5)	115.6	115.9	115.9	116.5
C(3)—N(4)—C(6)	125.0	125.0	125.1	125.2
C(1)—N(5)—C(6)	125.1	125.1	125.3	125.4
N(4)—C(6)—N(5)	116.0	115.9	115.6	115.3
α_2	2.9	−0.9	0.4	3.1
α_4	−0.9	0.7	0.0	−0.2
α_5	1.1	−0.4	−0.2	0.0
α_8	1.8	0.3	−0.4	1.6
α_9	0.8	0.1	0.1	1.5
α_{10}	0.0	0.1	0.1	−0.1
β_4	0.3	0.3	−0.2	0.8
β_5	2.1	−0.1	0.6	1.0
φ**	8.7	14.3	−4.5	7.5

* Bond lengths are given in Å, angles are in degrees.
** H—P(7)—C(2)—C(1) torsion angle for molecules **1a—1** and C_{Me}—P(7)—C(2)—C(1) for molecule **1d**.

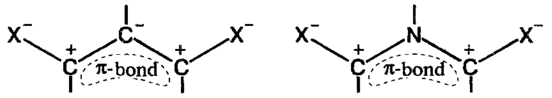
In all molecules under consideration we observe the shortening of the =C—C= bonds and the lengthening of the C=O bonds as compared to the sums of the covalent radii of their atoms. Meanwhile, the =C—C= bond length equals 1.446 and 1.429 Å in the **1a—1d** and **2a—2d** molecules, respectively, *i.e.*, it falls within the range between the standard value of 1.48 Å and the value of 1.395 Å of the C$\overset{...}{=}$C bond in aromatic compounds. The shortening of the N=C bonds is expressed more clearly in the **2a—2d** molecules than in the **1a—1d** derivatives.

The most stable is the eclipsed e_H-form with the smallest steric hindrances, though the difference between its energy and the energy of the e_{CH_3}-conformation is small (within 3.5 kcal mol^{-1}). Note that the advantage of the e_H-form was also proved, for example, in the case of the thymine molecule using the more stringent methods of calculation.[4]





The structural effects under consideration correspond to the phenomenological concepts on the bond nature in phosphoranylidenes.[6] Within the scope of these concepts, the P=C bond is semipolar $-\overset{+}{\underset{/}{\overset{\backslash}{P}}}{=}\overset{-}{C}<$, and the unshared electron pair (UEP) of the $>\overset{-}{C}-$ ion is involved in conjugation with the neighboring C=X bonds, which are strongly polarized (Fig. 1), thus forming a three-centered π-bond that provides the planarity of the X(8)=C(1)—C(2)—C(3)=X(9) fragment. Similarly, the UEP of the N atoms



with the planar bond configuration are conjugated with the neighboring C=X bonds resulting in the three-centered π-bonds that provide the planarity of the X(9)=C(3)—N(4)—C(6)=X(10) and X(8)=C(1)—N(5)—C(6)=X(10) fragments and the whole cycle. These three-centered bonds, which overlap at the C=X groups, form a pseudoaromatic π-system resembling the π-system of benzene derivatives.

The analysis of shortening effects of the =C—C= and N=C— bonds (see Tables 1 and 2) enables one to suppose that the n,π-conjugation in pseudoaromatic molecules results only in a slight disturbance of UEP at the $>\overset{-}{C}-$ and $-N<$ centers that is expressed by the

Table 2. Main geometric parameters of molecules **2a—2d**

Parameter*	Molecule			
	2a	**2b**	**2c**	**2d**
C(1)—C(2)	1.427	1.427	1.428	1.429
C(2)—C(3)	1.428	1.427	1.428	1.434
C(3)—N(4)	1.400	1.402	1.404	1.402
C(1)—N(5)	1.400	1.399	1.400	1.406
N(4)—C(6)	1.397	1.397	1.394	1.392
N(5)—C(6)	1.398	1.395	1.397	1.391
C(2)—P(7)	1.696	1.706	1.716	1.739
C(1)=S(8)	1.589	1.590	1.593	1.590
C(3)=S(9)	1.588	1.589	1.590	1.593
C(6)=S(10)	1.577	1.579	1.579	1.579
C(1)—C(2)—C(3)	123.2	123.2	122.4	121.0
C(2)—C(3)—N(4)	115.3	116.0	115.6	116.4
C(2)—C(1)—N(5)	115.2	115.2	115.8	116.0
C(3)—N(4)—C(6)	125.7	125.7	125.9	126.2
C(1)—N(5)—C(6)	125.7	126.4	125.8	126.6
N(4)—C(6)—N(5)	115.0	114.4	114.6	113.8
α_2	0.0	−0.1	0.1	−3.2
α_4	−0.3	0.5	−0.1	0.1
α_5	0.1	0.1	0.0	0.5
α_8	0.1	0.3	0.0	−1.9
α_9	0.0	0.2	0.0	−1.6
α_{10}	0.0	0.4	0.0	0.1
β_4	−0.1	0.1	0.0	−0.5
β_5	0.1	0.3	0.0	−0.8
φ**	−0.5	29.5	−0.25	−6.0

* Bond lengths are given in Å, angles are in degrees.

** H—P(7)—C(2)—C(1) torsion angle for molecules **2a—2c** and C_{Me}—P(7)—C(2)—C(1) for molecule **2d**.

Table 3. Main geometric parameters of molecules **1e**, **1f**, and **2e**

Parameter*	Molecule		
	1e X = O	**1f** X = O	**2e** X = S
C(1)—C(2)	1.450	1.446	1.433
C(2)—C(3)	1.448	1.445	1.433
C(3)—N(4)	1.428	1.422	1.406
C(1)—N(5)	1.425	1.423	1.406
N(4)—C(6)	1.402	1.405	1.393
N(5)—C(6)	1.403	1.405	1.393
C(2)—P(7)	1.731	1.691	1.740
C(1)=X(8)	1.238	1.236	1.591
C(3)=X(9)	1.236	1.236	1.591
C(6)=X(10)	1.231	1.230	1.580
C(1)—C(2)—C(3)	120.0	122.4	119.8
C(2)—C(3)—N(4)	116.0	115.6	115.9
C(2)—C(1)—N(5)	116.9	115.8	115.8
C(3)—N(4)—C(6)	125.8	125.2	126.1
C(1)—N(5)—C(6)	124.8	125.0	126.0
N(4)—C(6)—N(5)	115.1	115.9	113.8
α_2	11.8	−2.2	16.9
α_4	−1.3	0.1	−2.9
α_5	0.4	−1.2	−0.7
α_8	6.4	−1.3	10.2
α_9	6.2	−0.8	8.9
α_{10}	−0.9	−0.2	−1.4
β_4	2.2	−1.1	2.9
β_5	7.1	2.1	4.8
φ**	−79.7	78.2	−89.3

* Bond lengths are given in Å, angles are in degrees.

** R^1—P(7)—C(2)—C(1) torsion angle (R^1 = Et in molecules **1e** and **2e**; R^1 = Ph in molecule **1f**).

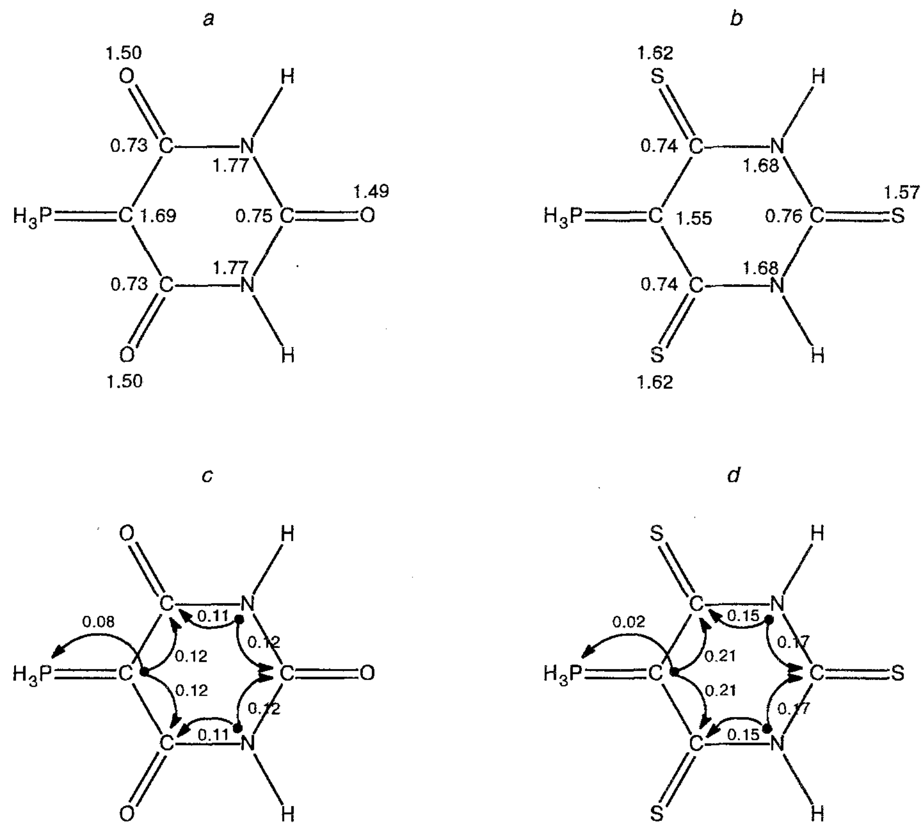


Fig. 1. Calculated π-electron occupations of atoms in molecules **1a** (*a*) and **2a** (*b*). The estimated electron shifts accounted for by the UEP conjugation at the C and N centers with the C=O (*c*) and C=S (*d*) bonds; the π-electron density shift toward the $-\!\!\!>\!P^{\pm}-$ center displayed in the diagram is interpreted nowadays as the effect of n,σ-hyperconjugation of the UEP at $>\bar{C}-$ with the $\mathrm{H}-\!\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{>}}\!\mathrm{P}^{\pm}-$ bonds.

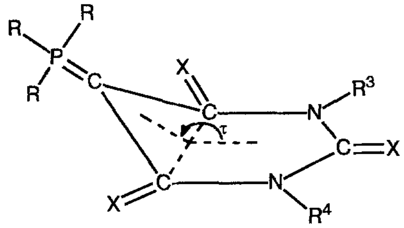
duffuse peripheral parts of their charge clouds. In other words, the pseudoaromatic π-system is composed of three diffuse UEP at $>\bar{C}-$ and $-N<$ and only slightly involves the neighboring atoms in the cycle (see Fig. 1). Therefore, it is reasonable to expect that the rigidity of a pseudoaromatic cycle with respect to planar and/or nonplanar deformations would be significantly smaller than the rigidity of an aromatic ring in benzene derivatives.

The introduction of substituents that produce steric hindrances in the neighborhood of the C(2), N(4), and N(5) atoms may make them deviate from the cycle plane. In this case, the angle of atomic deviation corresponds to the equilibrium between the forces of the steric effect of substituents on the neighboring carbonyl or thiocarbonyl groups, on the one hand, and the reaction of the pseudoaromatic π-system on the distortion in the cycle planarity that weakens the n,π-conjugation, on the other hand. A similar effect can be observed in the presence of electronegative substituents at the nitrogen atom, which increase the degree of pyramidicity of its bonds.

We should begin the discussion of the effects of susbstituents with a consideration of substitution at the phosphorus atom in the standard molecules of **1a** and **2a**. When replacing hydrogen atoms in molecule **1a** by ethyl groups (**1e** molecule: $R^1 = R^2 =$ Et, $R^3 = R^4 =$ H; Table 3), the e_R-conformation, which is characteristic of compounds **1a—1d** without steric hindrances, becomes unstable, and the molecule takes the orthogonal (o_R) form, where the axis of one $=\overset{|}{\underset{|}{P}}-$Et bond is orthogonal to the cycle plane and the two others are above the first one. The interaction of the substituents situated above the plane with the C(1)=O(8) and C(3)=O(9) carbonyl groups lengthens the distances between the adjacent atoms leading the C(2) atom from the cycle plane toward these substituents; meanwhile, the C(1) and C(3) atoms retain their planar configuration that results in the deviation of the O(8) and O(9) atoms in the opposite direction (with respect to C(2)).

This description of the steric effects of substituents at the phosphorus atoms indicates also the main structural features of molecule **2e** (see Table 3). In this case, o_R-conformation is the most stable that agrees also with the calculated geometric parameters of molecule **1f** (R^1 = Ph, R^2 = R^3 = R^4 = H; see Table 3) having the o_{Ph}-form. The part of substitients above the plane is taken by hydrogen atoms, which have the small van der Waals radii and produce no noticeable effect on the structure of the pseudoaromatic cycle.

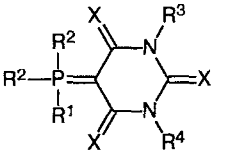
Generalizing the data mentioned above, we may suppose that molecules of the following type



R^3 = R^4 = H, Me
R = Et, Ph, Bu^t, *etc.*

have the o_R-form with a nonplanar pseudoaromatic cycle, where the τ angle, which characterizes its conformation, ranges from 160 to 170° depending on the nature of the R substituent.

Molecules of the following type



R^2 = R^3 = R^4 = H, Me
R^1 = Et, Ph, Bu^t

shall be characterized by the o_{R1}-form with a planar (or nearly planar) pseudoaromatic cycle. Note that our predictions relate to the gas phase, where the structure is determined by intramolecular interactions. However, the X-ray diffraction study of the derivative of acid **1** with R^1 = R^2 = Ph; R^3 = R^4 = Et carried out by I. A. Litvinov and O. N. Kataeva (unpublished data) gave a τ value of *ca.* 167° that agrees well with the given estimations.

The steric effects of substituents at the nitrogen atoms are considered by an example of molecule **1g** (R^1 = R^2 = R^3 = H, R^4 = Bu^t; Table 4). When introducing of *tert*-butyl group at the N(4) atom, its bonds retain their planar configuration, and Bu^t takes the o_{CH_3}-configuration, which is sterically more advantageous. The interaction of methyl groups below the cycle plane with the C(3)=O(9) and C(6)=O(10) groups shifts the N(4) atom under this plane, *i.e.*, toward the methyl groups affecting the oxygen atoms. The deviation of the N(4) atom from the plane of cycle occurs in such a way that the C(3) and C(6) atoms retain the planar bond configuration. Thus, the steric effect of *tert*-butyl group on the geometry of a pseudoaromatic cycle is described by the same regularities as the effect of substituents at the phosphorus atom.

Table 4. Main geometric parameters of molecules **1g** and **1h**

Parameter*	Molecule	
	1g	**1h**
C(1)—C(2)	1.444	1.445
C(2)—C(3)	1.451	1.444
C(3)—N(4)	1.444	1.462
C(1)—N(5)	1.419	1.419
N(4)—C(6)	1.428	1.445
N(5)—C(6)	1.413	1.401
C(2)—P(7)	1.679	1.683
C(1)=O(8)	1.235	1.236
C(3)=O(9)	1.233	1.231
C(6)=O(10)	1.227	1.225
C(1)—C(2)—C(3)	122.2	123.1
C(2)—C(3)—N(4)	115.9	115.6
C(2)—C(1)—N(5)	114.2	115.8
C(3)—N(4)—C(6)	114.9	122.0
C(1)—N(5)—C(6)	123.8	125.8
N(4)—C(6)—N(5)	115.4	116.1
α_2	9.2	0.4
α_4	−36.9	−13.2
α_5	−2.3	−1.2
α_8	1.8	0.1
α_9	−13.5	2.5
α_{10}	−19.8	1.9
β_4	−1.2	31.8
β_5	−9.6	0.0
φ**	−7.3	2.6

* Bond lengths are given in Å, angles are in degrees.
** H—P(7)—C(2)—C(1) torsion angle.

As is known, the degree of bond pyramidicity of the trivalent nitrogen atom depends significantly on the electronegativity of substituents. Therefore, one can expect that the electronegative substituent $R^{3(4)}$ at the N atom enhances the β angle corresponding to the given N atom and leads it out from the plane of cycle. The validity of this prediction is illustrated by the example of molecule **1h** (R^1 = R^2 = R^4 = H; R^3 = OH; see Table 4).

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