

Quantum-Chemical Investigation of Spatial and Electronic Structure of Verdazyl and its Derivatives

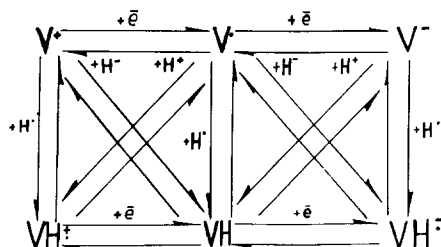
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Abstract

The unrestricted HF method in the INDO approximation with optimized geometry was used to describe the electronic structure of the hetero-ring of verdazyl and the derivatives of the latter. The results obtained are in good agreement with the experimental EPR spectra of triphenylverdazyl radical and its dipole moment. These data may be a basis for understanding and predicting the chemical properties and reactivity of verdazyl and its derivatives.

Verdazyl radicals [1] are widely used in solving the fundamental problems of theoretical organic chemistry and for practical purposes [2, 3]. They are among the most stable free radicals. Cations of verdazyls are comparatively stable and in some cases they can be separated in an individual state [4]; anions of verdazyls are only postulated as intermediate species in reactions of homolytic substitution by action upon triphenylverdazyl Grignard's reagents [5, 6] or by polarographic reduction of triphenylverdazyl [7]. In the simplest chemical reaction proceeding without any changes in their heteroring, the verdazyl radicals may undergo the following transformations:



The changes in spatial and electronic structure of the verdazyl radical and its ions are of great significance for understanding their reactivity in the reactions mentioned above.

In this paper we cite the results of quantum investigations of a model heteroring of the verdazyl radical (V·), its cation (V⁺) and anion (V⁻) by the INDO method with total geometry optimization [8]. These results make it possible to interpret some specific features of the electronic structure of these compounds and approach well-founded prognoses related to their reactivity.

Since in the conformational transition of heteroring the total energy, charge distribution, and bond length, as well as valence angles, change only slightly [8], all calculations were made for the "bath" conformer only.

The main results are shown in Figure 1 and Table I. Comparison of data [cf. Figs. 1(a-c)] shows that the row cation-radical-anion process undergoes substan-

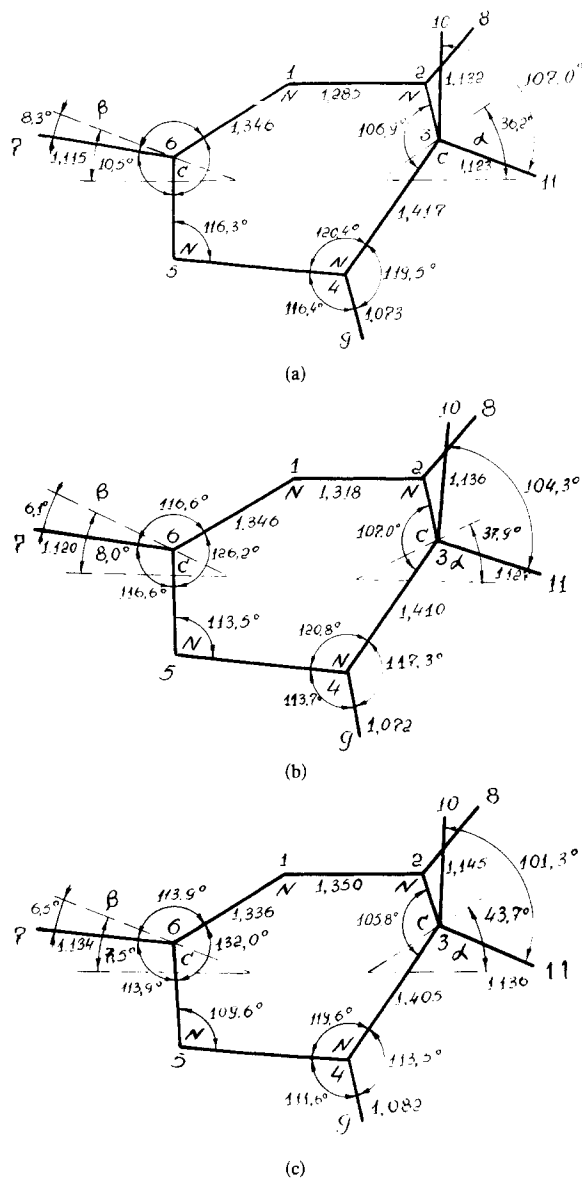


Figure 1. Spatial structure of cation (a), radical (b), and anion (c) of verdazyls.

TABLE I. Electronic structure of heterocycle of verdazyl and its ions.

	Cation	Radical	Anion
Total energy (a.u.)	-61.96887	-62.25905	-62.20621
E_{HOMO}	-0.6399	-0.3518 ^a	-0.0116
E_{LUMO}	-0.2242	0.1812 ^a	0.4436
Dipole moment	-	2.835	-
Charge on atom			
N ₁ (N ₅)	0.0945	-0.1360	-0.4125
N ₂ (N ₄)	0.0267	-0.0628	-0.1019
C ₃	0.2394	0.2770	0.2975
C ₆	0.0904	0.1776	0.2855
H ₇	0.0653	-0.0381	-0.1530
H ₈ (H ₉)	0.1765	0.0704	-0.0416
H ₁₀	-0.0141	-0.0961	-0.1687
H ₁₁	0.0238	-0.0634	-0.1494
Bond order ^b			
N ₁ —N ₂ (N ₄ —N ₅)	1.4073	1.1046	0.9828
N ₂ —C ₃	1.0017	1.0273	1.0552
N ₅ —C ₆	1.3964	1.3891	1.4763
Bond energy (a.u.)			
N ₁ —N ₂	-1.3521	-1.1879	-1.0363
N ₂ —C ₃	-1.0867	-1.1204	-1.1384
N ₅ —C ₆	-1.3312	-1.3428	-1.4201
Valency			
N ₁ (N ₅)	2.900	2.586	2.700
N ₂ (N ₄)	3.473	3.193	3.053
C ₃	3.938	3.953	3.950
C ₆	3.863	3.821	3.907

^aFor α spin.^bSee Ref. 13.

tional changes in N₁—N₂ (N₄—N₅) bond length: 1.285–1.318–1.350 Å; the other bond lengths change only slightly, i.e., less than 0.01 Å. In anions N₁—C₆ and N₂—C₃ bonds are shorter than in the radical. The enlarging of the N—N bond length in row cation-radical-anion results in a considerable weakening of these bonds and the corresponding increase in the polarity of heterocycles. Angle α in the same row rises from 36.2° to 43.7° and the angle for N₁C₆N₅ from 122.6° to 132°, while the distance of N₁—N₅ increases at the same time: 2.37–2.40–2.44 Å. The spatial data obtained are in good agreement with experimental x-ray data [9] (in parentheses): N₁—N₂, 1.318 Å (1.348 Å); N₁—C₆, 1.346 Å (1.337 Å); N₂—C₃, 1.410 Å (1.440 Å); angle α is 37.9° (42.9°), β is 8.0° (9.5°).

Since the experimental dipole moment (2.94 D) is very close to the calculated one (2.835 D), the main contribution to the total dipole moment was found to be associated with heteroring polarity [1]. Hyperfine coupling constants on nitrogen atoms are equivalent in pairs as was expected, differ only slightly ($\rho_{\text{N}_1}/\rho_{\text{N}_2} = 1.075$), and in INDO's standard deviation limits, agree with the experimental

values (calculated $a_N = 7.88$ and 7.33 g, respectively, with an experimental value of ≈ 6.0 g). It should be noted that spin densities on CH_2 -hydrogen atoms differ in value and as it was shown previously [8], have different signs for "chain" and "bath" conformers. Experimental values of the hyperfine coupling constant is about 0.03 g [10]; this may be due to the conformation transitions during which the sign of the hyperfine coupling constant changes.

In accord with the obtained values for the total energy of the investigated species (see Table I) their thermodynamical stability decreases in the row: $V^{\cdot} > V^{\cdot-} > V^{\cdot+}$. The formal charges on atoms decrease in the row: $V^{\cdot+} > V^{\cdot} > V^{\cdot-}$. However, there are surprisingly high positive charges on the carbon atoms. In accord with the "merostabilization" principle [11], one of the main causes of high stability of verdazyls is probably due to large contributions of highly polar structures to their ground state. It can be assumed that species with positively charged atoms in the third or sixth positions can form stable free "quasiverdazyl" radicals.

There should be particular stress on the high polarity of the verdazyl anion which is due to the fact that the neighboring atoms of carbon and nitrogen have large and different sign charges. The presence of such charges on probable reaction's centers should lead to the highest reactivity of the verdazyl anion. Although the anion is comparatively stable from the thermodynamic viewpoint, it is clear that its nucleophilic properties are much higher than those of the verdazyl radical. Since the reactivity of verdazyls is to a large extent associated with their high electron donating properties [12], it can be assumed that the high nucleophilicity of the anion's reaction centers results in the impossibility of its identification.

The data obtained are very helpful in interpreting the experimental results. These data may be a basis for understanding and predicting the chemical properties and reactivity of verdazyl and its derivatives.

Examination of the electronic structures of the verdazyl heteroring shows that their reactions can occur due to two reaction centers: (i) nitrogen atoms N_1 and N_5 , since they possess the greatest part of π electronic spin density and considerable negative charge (interaction with electrophilic reagents), and (ii) a carbon atom C_3 with a large positive charge (coordination of nucleophilic reagents to this center is possible). It is the presence of the two reaction centers in verdazyl's molecule and the possibility of formation of cyclic transition states that explain, for example, dehydrogenation reactions with *N*-benzyl-1,4-dihydronicotinamide and 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine [2], the reaction of oxidation of verdazyl by diacyl peroxides [14], and the cyclization of verdazyl heteroring when acting upon the verdazyl with bromodicyanomethane [15]. The assumption about the great role of constant or temporary ring formation in heterolytic reactions [16] is probably true for a large number of homolytic reactions (firstly in reactions of highly polar radicals) as well.

Proceeding from the obtained data prediction can be made about large decreases in verdazyl radical's reactivity in reactions with peroxy esters, peroxides, and hydroperoxides in comparison with diacyl peroxides. For example,

triphenylverdazyl in normal conditions does not react with *tert*-butyl peroxide, triphenylmethyl peroxide, and 2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-on peroxide, which is apparently due to a great decrease in nucleophilic properties of one of the reagent's centers. It can be assumed that in reaction with peroxyacids the energetic barrier of the reaction will increase.

Considerable positive charge on the carbon C₃ atom in the verdazyl cation causes the recyclization of these substances upon the action of small nucleophilic agents (—OH, —OPh) [2]. If there is a nucleophilic agent with volumetric substituents, the reaction is accompanied by electron transition to form the verdazyl radical as it happens in reactions with tetramethylparaphenylenediamine or with salts of sterically hindered phenols [17].

It should be noted that the possibility of some reagents through two reaction centers in verdazyl's reactions may be a very fruitful conclusion while studying the structure and reactivity of various stable polar radicals.

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