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Unrestricted Hartree-Fock-Roothaan Calculations of Geometrical Parameters of (*Z*)-$CH_3CH{=}NO^{\cdot}$ and (*E*)-$CH_3CH{=}NO^{\cdot}$ Iminoxy Radicals

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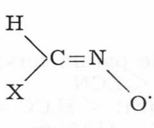
Equilibrium geometrical configurations of (Z)—$CH_3CH{=}NO^{\cdot}$ and (*E*)—$CH_3CH{=}NO^{\cdot}$ radicals were estimated at UHF/6-31G* level, correlation corrections of bond length being taken into account. It was found that in the formation of iminoxy radicals from parent (Z)—$CH_3CH{=}NOH$ and (*E*)—$CH_3CH{=}NOH$ diamagnetic molecules the $=N—O^{\cdot}$ bond length decrease by ~ 0.15 Å, $>C{=}N—O^{\cdot}$ angle increases by $\sim 10^{\circ}$, geometrical configuration of $CH_3CH{=}N—$ fragment being altered insignificantly.

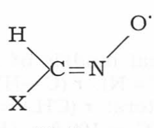
The barrier of inner rotation of (*E*)—$CH_3CH{=}NO^{\cdot}$ radical is shown to be equal to ~ 1.5 kcal/mol. The rotation about the C—C bond in (Z)—$CH_3CH{=}NO^{\cdot}$ radical is in fact unhindered.

INTRODUCTION

Monosubstituted $XCH{=}NO^{\cdot}$ iminoxy radicals exist in two diastereomeric forms which convert into each other due to the inversion of iminoxy group.



(Z)-form



(*E*)-form

In accordance with ESR investigations of the iminoxy radicals in solution the inversion of $>C{=}NO^{\cdot}$ group is hindered and it is a slow process relative to the ESR time scale.[1,2] In the solution of $XCH{=}NO^{\cdot}$ iminoxy radicals there is equilibrium between (*Z*) and (*E*) isomeric forms, which often have close values of free energies and are present in the equilibrium mixture in commensurable amounts.[2] As the assignment of the observed ESR spectra to (*Z*) and (*E*) isomeric forms of $XCH{=}NO^{\cdot}$ is as a rule ambiguous,[3] the question about the preferable stability of diastereomers is far from being settled. Provision of reliable experimental data concerning the geometrical configurations of iminoxies is connected with serious difficulties. Nowadays such data are not available in literature. Nonempirical Hartree-Fack-Roothaan method, being a reasonable alternative to the experiment, gives a fairly accurate estimation of molecular geometrical parameters.

Equilibrium configurations of $H_2C{=}NO^{\cdot}$, (*Z*)-$FCH{=}NO^{\cdot}$ and (*E*)—$FCH{=}NO^{\cdot}$ have been determined earlier.[4] In the present paper the geometries of (*Z*)-$CH_3CH{=}NO^{\cdot}$ and (*E*)—$CH_3CH{=}NO^{\cdot}$ are calculated and the potentials of the inner rotation about C—C bond are determined.

Methods. Basis sets

Equilibrium geometrical parameters of (*Z*)-$CH_3CH{=}NO^{\cdot}$ and (*E*)—$CH_3CH{=}NO^{\cdot}$ have been calculated by the UHF/6-31G method. The values of r (N—O), r (C=N) bond lengths and $\rangle$C=N—O$^{\cdot}$ valence angle have been refined later at the UHF//6-31G* level. Geometry optimization was performed by the Pulay-Schlegel gradient method as implemented in the MONSTERGAUSS-81 program.[5] Geometrical models of the radicals under study are presented in Figure 1.

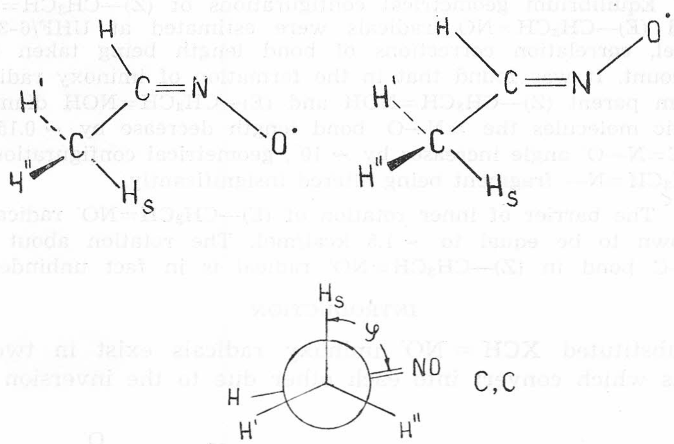


Figure 1. Geometrical models of $CH_3CH{=}NO^{\cdot}$ radical. Variable parameters: r (N—O), r (C=N), r (C—H), r (C—C); $<$ CNO, $<$ HCN, $<$ CCN
Assumed parameters: r (CH_s) = r (CH′) = r (CH″) = 1.09 Å; (*Z*): $<$ H_sCC = 111.4°; $<$ H′CC = 109.9°; (*E*): $<$ H_sCC = 110.4°; $<$ H′CC = 110.5°.[6]

Error Estimations

Errors in equilibrium bond lengths and valence angles have been estimated according to the following assumptions:

1. Errors in the calculated value of the M-X bond length may be conditionally divided into »systematic« and »accidental« ones. Δr_s (M-X) systematic error depends only upon the type of M-X bond and it may be considered as an additional correction of the calculated r (M-X) value. Δr_s (M-X) value at the UHF/6-31G* level of calculation coincides with the Δr_c (M-X) correlation correction, taking into account the effect of electron correlation on the (M-X) equilibrium bond length. Correlation corrections of $=C<_{H}$ and $\rangle$C=N bond lengths equal 0.010 Å and 0.025 Å, respecti-

vely.[4] The correlation correction to =N—O˙ and C—C bonds are assumed to be equal to zero.[4] Δr_a (M-X) accidental error depends upon the environment of the M-X bond in the molecule under study. The largest deviation of r_{calc} (M-X) + + Δr_s (M-X) from experimental r (M-X) value in the series of molecules containing the bond in question may serve a quantitative measure of Δr_a (M-X). Δr_a value determined at the UHF/6-31G* level does not exceed 0.02 Å for all types of bonds of the $CH_3CH=NO^{\cdot}$ radical.[4]

2. Errors in calculations of >C—C(—)=N—, H—C(—)=N and >C=N—O˙ valence angles do not exceed 2°.[4]

3. The effect of polarization functions on C—C and =C<H bond lengths and >C—C(—)=N— and H—C(—)=N bond angles is negligible.

Error estimations carried out in accordance with (1—3) are rather disputable. Nevertheless we hope this approach gives a true idea about the accuracy of the performed calculations. This approach has already been discussed in some detail.[4]

RESULTS AND DISCUSSION

Monosubstituted iminoxies are formed from the parent oximes in the course of the homolytic scission of hydroxyl group, the bond configuration at N atom remaining unaltered.[2] Due to this fact it is interesting to answer the following questions:

1. Is the relative stability of the (*Z*) and (*E*) forms of $CH_3CH=NOH$ molecule conserved in the elimination of hydroxyl hydrogen and in the formation of radical?

2. Is the effect of electronegative substituent on the >C=NOH and >C=NO˙ geometrical parameters the same in both cases?

(*Z*)-$CH_3CH=NOH$ and (*E*)—$CH_3CH=NOH$ geometrical configurations were determined by Nguen and Ha[6] at the HF/DZHD level (DZHD — double ζ basis set of Huzinaga and Dunning). The values of bond lengths and valence angles were calculated,[6] along with the equilibrium configurations of (*Z*)—$CH_3CH=NO^{\cdot}$ and (*E*)—$CH_3OH=NO^{\cdot}$ are presented in Figure 2. Geometrical parameters of radicals in question are estimated using the data of Table I, correlation corrections to >C=N— and =C<H bond lengths being taken into account. Errors in the estimations of bond lengths and valence angles probably do not exceed 0.02Å and 2°, respectively (see the previous part of the paper).

As it can be seen from Figure 2, geometrical parameters of >C=NO˙ group in (*Z*) and (*E*) forms of $CH_3CH=NO^{\cdot}$ radical coincide in the range of 0.005Å and 1°. The same result has been obtained for (*Z*)—$FCH=NO^{\cdot}$ and

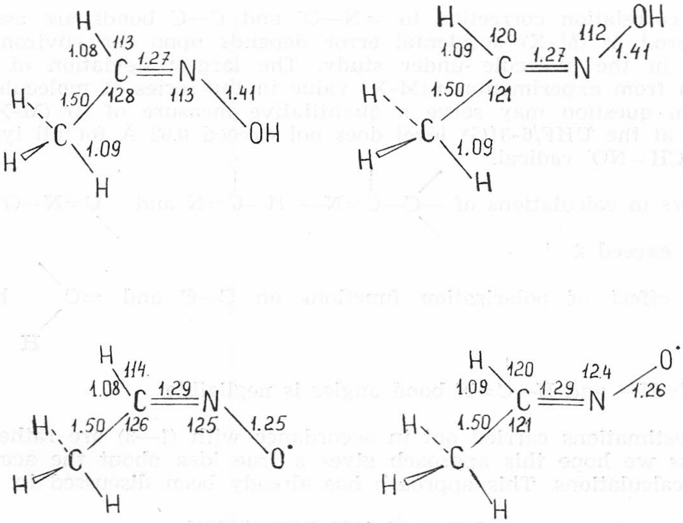


Figure 2. Equilibrium geometrical parameters of (Z)—$CH_3CH{=}NOH$ and (*E*)—$CH_3CH{=}NOH$ oximes[6] and (Z)—$CH_3CH{=}NO^{\cdot}$ and (*E*)—$CH_3CH{=}NO^{\cdot}$ iminoxy radicals (bond lengths in Å; valence angles in degrees).

(*E*)—$FCH{=}NO^{\cdot}$ radicals.[4] In the iminoxy radical formation from the parent oximes the $=N—O^{\cdot}$ bond length decreases by ~0.15 Å, while the $C{=}N—O^{\cdot}$

TABLE I

UHF optimized geometrical parameters of (Z) and (E) forms of $CH_3CH{=}NO^{\cdot}$ radical ($\varphi = 0^{\circ}$)

		(Z)—$CH_3CH{=}NO^{\cdot}$		(*E*)—$CH_3CH{=}NO^{\cdot}$	
		6-31G	6-31G*	6-31G	6-31G*
r (NO)	(A)	1.295	1.251	1.299	1.257
r (CN)	(A)	1.291	1.274	1.292	1.275
r (CH)	(A)	1.070	1.070‡	1.076	1.076‡
r (CC)	(A)	1.503	1.503‡	1.496	1.496‡
< CNO	(°)	124.6	125.0	123.3	123.6
< HCN	(°)	114.5	114.5	120.4	120.4‡
< CCN	(°)	126.3	126.3‡	120.6	120.6‡
$\langle S^2 \rangle$		1.04	0.96	1.05	0.97
E_{tot} (at. un)		—207.18641	—207.28072	—207.18656	—207.28072

‡ Not reoptimized.

angle increases by ~10°, the geometrical configurations of $CH_3CH{=}N$— being altered insignificantly. It may be mentioned thata small increase of $r\,(C{=}N)$ takes place, as well as that in the other radicals studied.

Geometrical configurations of iminoxy group in $H_2C{=}NO^{\cdot}$ and $CH_3CH{=}{=}NO$ coincide with the accuracy of the 0.01 Å and 1°. The substitution of the methyl group for electronegative fluorine atom leads to a decrease of

$>$C=N— bond by 0.03 Å. The same effect may be observed in a series of relative diamagnetic oximes.[6] Variations of the =N—O$^{\cdot}$ bond lengths and $>$C=N—O$^{\cdot}$ valence angles in the row of $CH_3CH=NO^{\cdot}$, $FCH=NO^{\cdot}$ do not exceed 0.02 Å and 2°, respectively.

In accordance with[6] the (*E*) form of $CH_3CH=NOH$ molecule is more stable than the (Z) form by 0.6 kcal/mole (HF/DZHD). It can be seen from Table I that the energies of $CH_3CH=NO^{\cdot}$ diastereomeric forms coincide with the accuracy of 0.005 kcal/mole (UHF/6-31G*).

The potential of the inner rotation of $CH_3CH=NO$ radical may be presented as a row

$$V(\varphi) = 0.5 \sum_{K=1}^{\infty} v_{3k} (1 - \cos 3k\varphi). \tag{1}$$

It is usually assumed [7] that v_{3k} coefficients diminish rapidly at $K \to \infty$, and $V(\varphi)$ may be approximated by a one- or two-term sum of the series. In this approach the height of the inversion barrier coincides with the v_{3k} value, the coefficient influencing only the form of the barrier. The $V(\varphi)$ values at $\varphi = m \cdot 20^{\circ}$ (m = 0, 1, 2) were calculated by the UHF/6-31G* method. The calculations were performed at a fixed value of C—C bond length, geometrical parameters of $—CH=NO^{\cdot}$ group being taken from Table I (UHF/6-31G*). Methyl geometrical parameters in conformations with $\varphi = 20^{\circ}$ and $\varphi = 40^{\circ}$ were estimated by linear interpolation. The calculated values of $V(\varphi)$ were interpolated by the two-term sum of series (1); the coefficients of interpolation polynomial are given below (in kcal/mole)

(Z)—$CH_3CH=NO^{\cdot}$	$v_3 = 0.20$	$v_6 = -0.06$
(*E*)—$CH_3CH=NO^{\cdot}$	$v_3 = 1.49$	$v_6 = -0.05$

It is interesting to note that the barrier of inner rotation of $CH_3CH=NO^{\cdot}$ (*E*) form is approximately seven times as high as the barrier of (Z) form. In the case of (Z) isomer the rotation about C—C bond is in effect unhindered. The same results have been obtained earlier for (*E*) and (Z) isomers of butene-2.[8]

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SAŽETAK

Proračun geometrijskih parametara (Z)—$CH_3CH=NO^{\cdot}$ i (E)—$CH_3CH=NO^{\cdot}$ radikala primjenom neograničene Hartree-Fock-Roothaanove metode

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Ravnotežne geometrije radikala (Z)—$CH_3CH=NO^{\cdot}$ i (E)—$CH_3CH=NO^{\cdot}$ određene su metodom UHF/6-31G*. Uzet je u obzir i utjecaj korelacije elektrona. Razmatrane su karakteristike geometrijskih parametara i određene barijere unutrašnjih rotacija.