

The Molecular Structure of Pyruvaldehyde-1-oxime Determined by Gas Phase Electron Diffraction

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The molecular structure of pyruvaldehyde-1-oxime (oximinoacetone) has been determined by gas phase electron diffraction. The molecule exists in the *syn s-trans* form and there is no evidence of deviation from heavy atom coplanarity. C_{sv} symmetry was assumed for the methyl group. The root mean-square amplitudes of vibration and the perpendicular amplitude correction coefficients were calculated from an approximate valence force field. The following values were found for the more important bond distances and angles:

$R(C-CH_3) = 1.513(6)$ Å, $R(C=O) = 1.212(3)$ Å,
 $R(C-C) = 1.479(4)$ Å, $R(C=N) = 1.260(4)$ Å,
 $R(N-O) = 1.382(4)$ Å, $\angle CCC = 118.4(3)^\circ$, \angle
 $CCO = 118.4(4)^\circ$, $\angle CCN = 120.5(5)^\circ$ and $\angle CNO$
 $= 112.3(4)^\circ$.

Values in parentheses are standard deviations obtained by the least-squares method and they are not corrected for systematic errors. The parameters are consistent with the R_x structure.

Pyruvaldehyde-1-oxime (oximinoacetone) can exist in two isomeric forms because of the C=N bond. Throughout this article the configurational isomers will be denoted by the prefix *syn* and *anti*, in which the hydroxyl group is in *cis* and *trans* position to the methine proton, respectively. In this oxime with conjugated double bonds one can expect restricted rotation around the central C-C bond. This gives in addition conformational isomerism. Under the assumption of a planar NCCO skeleton four different forms can be distinguished (Fig. 1).

The compound has been subjected to configurational¹⁻⁴ and conformational studies.⁵ The fact that only one isomer is known hindered the assignment of the configuration. Kimura

*et. al.*² inferred by means of infrared spectroscopy that intramolecular hydrogen bonding, which is only possible in the *anti* isomer could be excluded. Mosher *et al.*³ came to the opposite conclusion. Attempts to interpret the magnitude of the chemical shifts of the methine and hydroxyl protons also led to contradictory results.^{2,3} The *syn* form was mentioned by Somin and Gindin,⁴ who used the stereospecific geminal spin-spin coupling of ¹⁵N=CH. Pigenet *et. al.*⁵ concluded from dipole moment measurements and the results of their ¹H NMR work, that the *syn s-trans* form is the most likely one.

Until now, no structural studies in the gas phase have been published. The aim of this work is to elucidate the molecular structure and to give a contribution to the discussion about the preferred forms of α,β -unsaturated oximes.^{5,7}

Besides, the investigation seemed interesting in connection with the studies on the length of the central C-C single bond in conjugated systems like glyoxal,⁸ acrolein,^{8,9} and butadiene,^{8,10} which indicate a dependence on the electronegativities of the substituents to which the carbon atoms are doubly bonded.

EXPERIMENTAL AND CALCULATION PROCEDURE

Pyruvaldehyde-1-oxime was obtained from Schuchardt and was purified by repeated sublimation (m.p. 67–68°C).

Diffraction photographs were taken on the Oslo apparatus.¹¹ The nozzle temperatures were about 85°C and the electron wavelength was 0.064580 Å, corresponding to an acceler-

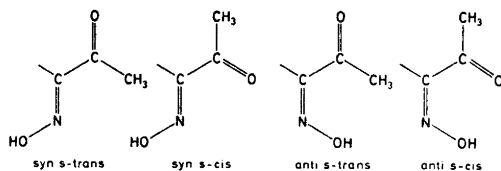


Fig. 1. The four forms of pyruvaldehyde-1-oxime with a planar heavy atom skeleton.

ating voltage of about 36 kV. Five and three plates, for which the camera distances were 480.56 and 200.56 mm, respectively, were selected for the structure investigation.

The plates were photometered and the data processed in the usual way.¹² The 48 cm data covered a range from $s=1.50$ to $s=18.75 \text{ \AA}^{-1}$ with $\Delta s=0.125 \text{ \AA}^{-1}$ and the 20 cm data from $s=6.25$ to $s=40.75 \text{ \AA}^{-1}$ with $\Delta s=0.25 \text{ \AA}^{-1}$. Scattering factors were calculated for 35 kV electrons using the partial wave method.¹³ The calculations were based on Hartree-Fock potentials.¹⁴ The backgrounds

were drawn on the leveled intensity curves and the molecular intensities obtained were modified by $s/|f_N'|/|f_C'|$. Background adjustment on the single curves was achieved by comparing the modified experimental intensities with the intensities calculated for the final model. The modified experimental intensities were scaled and averaged according to the methods described by Seip *et al.*,¹⁵ giving a set of data for each of the camera distances. The average correlation coefficient and the standard deviations at each point were calculated. A non-diagonal weight matrix¹⁵ was applied in the final least-squares refinements. The non-diagonal elements in the weight matrix were -0.6 and 0.11 for the 48 cm and -0.6 and 0.115 for the 20 cm data. The constants w_2 , s_1 , w_2 and s_2 for the diagonal part of the weight matrix¹¹ were 4.5, 5.5, 0.047, and 10.0 and 1.0, 11.0, 0.014, and 25.0, respectively. The curves were given equal weight with respect to each other.

The molecular intensities, together with the differences between experimental and theoretical intensities are represented in Fig. 2. The

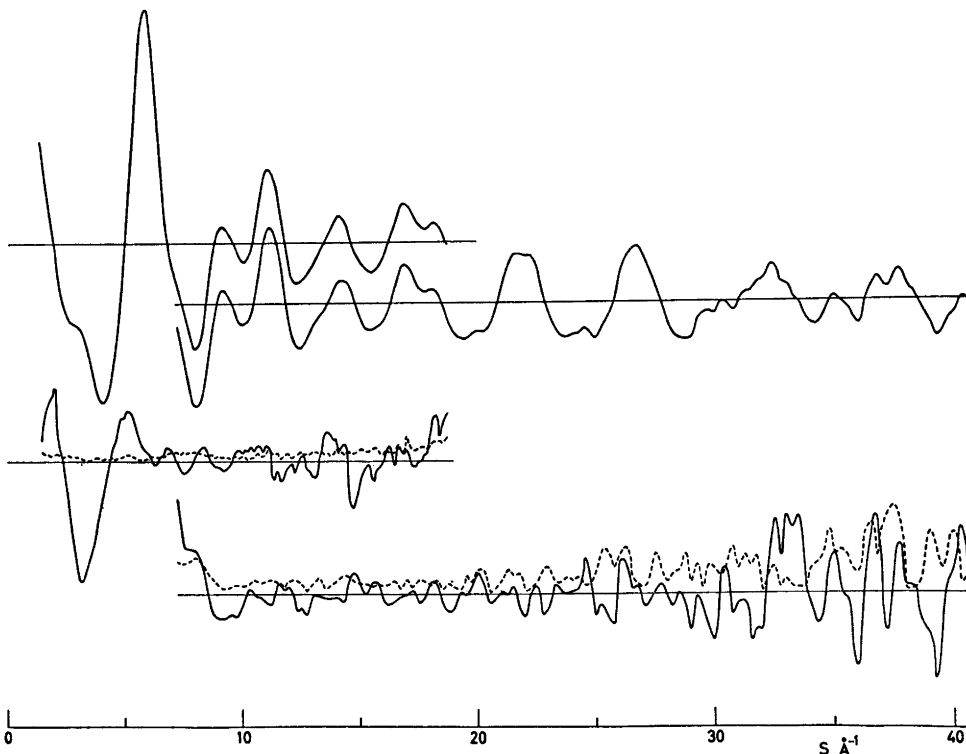


Fig. 2. The two upper curves represent the $s/|f_N'|/|f_C'|$ -modified experimental intensities of pyruvaldehyde-1-oxime for the 48 cm camera distance from $s=1.50$ to $s=18.75$ with $\Delta s=0.125 \text{ \AA}^{-1}$ and for the 20 cm distance from $s=6.25$ to $s=40.75$ with $\Delta s=0.25 \text{ \AA}^{-1}$. The two lower curves are the differences between the experimental and calculated intensities for the parameters given in column C of Tables 1 and 2 (solid curves) and the standard deviations of the averaged intensities (dashed curves). The standard deviations and the differences were multiplied by a factor of 5.

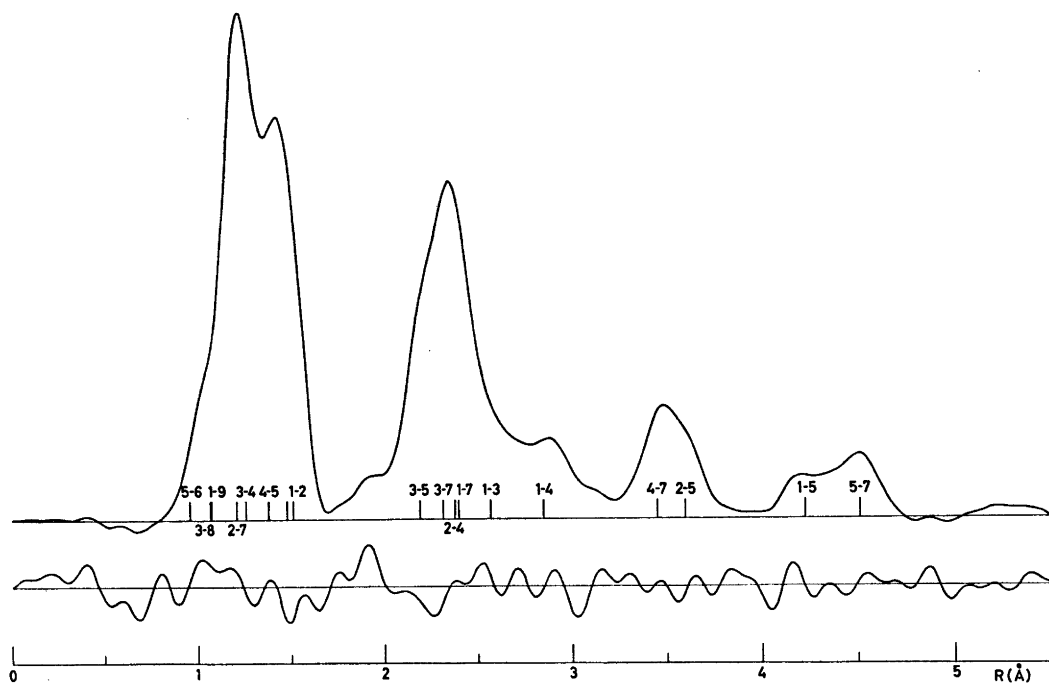


Fig. 3. Experimental radial distribution function for pyruvaldehyde-1-oxime and the differences between experimental and calculated functions. The differences were multiplied by a factor of 5. For the experimental function, calculated intensities were added inside $s = 6 \text{ \AA}^{-1}$ and the intensities were multiplied by a damping function of $(\exp -0.0015 s^2)$ before the Fourier inversion.

large differences at small s -values for the 48 cm data could not be removed by a smooth background correction. In fact, the weighting scheme does not reflect the experimental uncertainties in this region. It gives a very little weight below $s = 5.0 \text{ \AA}^{-1}$.

Radial distribution functions (Fig. 3) were calculated by Fourier inversion of the experimental and theoretical intensity curves after multiplication with an artificial damping function of $\exp(-0.0015s^2)$. For the experimental function, calculated intensities for the final model were added inside $s = 6.0 \text{ \AA}^{-1}$.

STRUCTURE ANALYSIS

With parameters obtained from related compounds radial distribution functions were calculated for the four forms with a planar heavy atom skeleton (Fig. 1). The agreement between experimental and theoretical functions was very poor for the forms with the *anti* configuration. There were significant differences in the region with short non-bonded distances from 2.1 to 2.8 Å. In addition a

peak is definitely apparent at $\sim 4.5 \text{ \AA}$ in the experimental function, which could not be obtained with reasonable values for bond distances and angles.

After adopting the *syn* configuration it was more difficult to decide whether there is a conformational equilibrium and which conformation is preferred. Most of the peaks in the radial distribution function are composite and with the initial parameters no basic differences between the two models could be detected. Preliminary least-squares refinements made the features of the models more distinct. Converged solutions for the *s-cis* model showed substantial disagreement between experimental and theoretical radial distribution functions and unreasonable values for the parameters. The refinements for the *s-trans* model gave directly better results and a satisfying agreement with the experimental data was obtained. Therefore, the *syn s-trans* form with a planar heavy atom skeleton and C_{3v} symmetry for the methyl group was chosen as

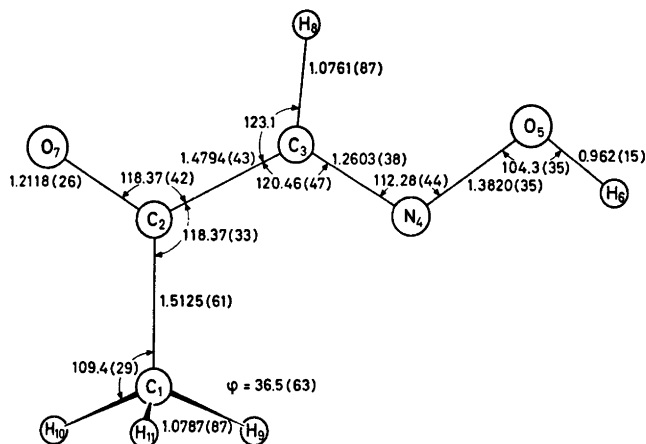


Fig. 4. The numbering of the atoms for pyruvaldehyde-1-oxime and final parameters from column C of Table 1. The bond distances are given in Å and the angles in degrees. The numbers in parenthesis are standard deviations, not corrected for systematic errors. ϕ is the dihedral angle $\phi(\text{H}_9\text{C}_1\text{C}_2\text{C}_3)$.

the final model. The atom numbering is shown in Fig. 4.

The mean amplitudes of vibration (u) and the perpendicular amplitude correction coefficients (K) at 85 °C were computed from an approximate valence force field using a modified¹⁶ computer program by Gwinn.¹⁷ The structural parameters used in this calculation are listed in column A of Table 1. Most of the force constants were transferred from related compounds such as acetone¹⁸ and acetaldoxime.¹⁹ Some force constants were adjusted to get a better fit between observed and calculated frequencies. Since only frequencies higher than 835 cm^{-1} have been reported²⁰ the torsional force constants had to be guessed. (The final force field data are available upon request.)

The results of three least-squares refinements are given in Tables 1 and 2; in Table 2 are also included the computed u - and K -values. For refinement A the given structure parameters correspond to R_a distances, while for refinement B and C R_α distances are given. To the approximation of small vibrations the two types of distances are related by²¹

$$R_\alpha + \langle \Delta z \rangle = R_a + u^2/R - K \equiv R_\alpha$$

For A the model was satisfied by the R_a distances, while in B and C the R_α distances fulfilled the geometry. The differences between the R_a distances C_1-C_2 and C_2-C_3 of the model,

$\Delta_{\text{C-C}}$, was in A and B set equal to zero and not varied.

Several attempts were made to refine $\Delta_{\text{C-C}}$ together with as many parameters as possible. By excluding the u -values of the bonded distances and fixing the $\text{C}_2\text{C}_3\text{H}_8$ angle on the value obtained in B, the results of C with a lower $V'PV$ were obtained. As expected some of the parameters were strongly correlated. The following terms of the moment matrix of the parameters were large

$$\begin{aligned} \rho[R_{\text{C}_1\text{C}_2}, \Delta_{\text{C-C}}] &= -0.96; \\ \rho[R_{\text{C}_2\text{N}_4}, \angle 3,4,5] &= -0.81 \\ \rho[R_{\text{N}_4\text{O}_5}, \angle 3,4,5] &= -0.74; \\ \rho[R_{\text{C}_2\text{N}_4}, u_{\text{N}_4\text{O}_5}] &= 0.76 \end{aligned}$$

In all the three refinements the u -values of distances involving hydrogen atoms were fixed on the computed values. The u -values which could be refined together with the geometrical parameters are given with standard deviations. To reduce the number of independent parameters, some of the u -values were collected in groups; the u -values belonging to the same group got the same least-squares shifts and the same standard deviations. The experimental u -values for the bonded distances given without standard deviations in Table 2, were refined without varying the geometrical parameters and starting from computed values.

Table 1. Least-squares results for the distances, angles and scale factors of pyruvaldehyde-1-oxime.

Distances in Å and angles in degrees. In A the structure parameters correspond to R_α distances, and for B and C R_α distances are given. For A the geometry was satisfied by the R_α distances, while in B the corresponding R_α distances fulfilled the geometry. The split parameter Δ_{C-C} was defined by $\Delta_{C-C} \equiv R_{a1-2} - R_{a2-3}$, and R_{1-2} and Δ_{C-C} were kept as independent parameters. In A and B Δ_{C-C} was set equal to zero and not varied. For B $\Delta_{C-C} = 0$ gives a difference of -0.0011 between the R_α distances from computed u - and K -values of Table 2.

For C Δ_{C-C} was varied and the geometry was satisfied by the R_α distances. These R_α distances are given.

The same weighting scheme including offdiagonal elements was applied in all the three refinements (see text). $K(48)$ and $K(20)$ are the scale factors for the data of the 48 and 20 cm camera distances.

The u -values for the same three refinements are given in Table 2.

| | A | B | C |
|-----------------------|-------------|-------------|-------------|
| R_{1-2} | 1.4951(17) | 1.4930(17) | 1.5125(61) |
| R_{2-3} | | 1.4941(17) | 1.4794(43) |
| $\Delta(C-C)$ | 0.0 | 0.0 | 0.0331(98) |
| R_{2-7} | 1.2139(30) | 1.2104(33) | 1.2118(26) |
| R_{3-4} | 1.2649(47) | 1.2593(50) | 1.2603(38) |
| R_{4-5} | 1.3839(39) | 1.3789(38) | 1.3820(35) |
| R_{5-6} | 0.985(15) | 0.958(16) | 0.962(15) |
| R_{2-8} | 1.0838(87) | 1.0725(88) | 1.0761(87) |
| R_{1-9} | 1.0938(87) | 1.0751(88) | 1.0787(87) |
| $\Delta(C-H)$ | 0.01 | | |
| $\angle 1,2,3$ | 118.76(42) | 118.54(39) | 118.37(33) |
| $\angle 3,2,7$ | 117.14(35) | 117.63(36) | 118.37(42) |
| $\angle 2,3,4$ | 119.47(54) | 120.26(55) | 120.46(47) |
| $\angle 3,4,5$ | 111.91(54) | 112.37(54) | 112.28(44) |
| $\angle 4,5,6$ | 102.8(33) | 105.1(36) | 104.3(35) |
| $\angle 2,3,8$ | 122.9(53) | 123.1(50) | 123.1 |
| $\angle 2,1,9$ | 109.9(31) | 111.9(34) | 109.4(29) |
| $\angle \phi$ | 37.6(63) | 35.1(63) | 36.5(63) |
| $K(48)$ | 99.19(242) | 98.16(239) | 98.13(202) |
| $K(20)$ | 103.16(498) | 101.23(492) | 102.02(428) |
| $V'PV \times 10^{-3}$ | 10.69 | 10.62 | 10.50 |

The difference between the R_α distances between C_1-H methyl and C_3-H_3 was assumed to be 0.01 Å. stadia in the analysis together with the most important parameters.

The atomic coordinates consistent with the refinement C are given in Table 3.

In the earlier refinements the methyl group was kept fixed in a position with one of the hydrogen atoms eclipsed with respect to the carbonyl oxygen atom. However, refinement of the torsional angle about the C_1-C_2 bond improved the agreement between experimental and theoretical radial distribution functions and $V'PV$ decreased with 6%. Although the dihedral angle $\phi(H_3C_1C_2C_3)$ was found to have a large standard deviation it was decided to include this parameter in the final refinements.

In order to test the assumption of a planar heavy atom skeleton, the torsional angle about the C_2-C_3 bond was refined during different

DISCUSSION

The result is that pyruvaldehyde-1-oxime exists mainly in the *syn s-trans* form. The agreement between the calculated and experimental radial distribution functions indicates that the concentration of any additional conformers present must be small. This is in agreement with the suggestions of Somin and Grindin⁴ and Pignet *et al.*⁵ based on NMR and dipole moment measurements.

The final test on the torsional angle about

Table 2. Least-squares results for the mean amplitudes of vibration for pyruvaldehyde-1-oxime, including u - and K -values calculated from an approximate valence force field at 85 °C.

Values for the root mean-square amplitudes of vibration, $u = \langle \Delta z^2 \rangle^{1/2}$ in Å, and the perpendicular amplitude correction coefficients, $K = (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle) / 2R$ in Å are given. The experimental u -values were obtained in refinement A, B, and C of Table 1, and the values with standard deviations were varied in these refinements. Some of the u -values were refined in groups. These have the same standard deviations.

| Distance | u (Å) A | B | C | Calc. | K (Å) |
|------------|--------------|-------------|------------|--------|---------|
| 1-2 | 0.0492(41) | 0.0477(41) | 0.0462 | 0.0488 | 0.0043 |
| 2-3 | | | | 0.0485 | 0.0031 |
| 2-7 | 0.0406 | 0.0409 | 0.0407 | 0.0393 | 0.0065 |
| 3-4 | 0.0419 | 0.0422 | 0.0420 | 0.0406 | 0.0054 |
| 4-5 | 0.0493(41) | 0.0470(41) | 0.0463 | 0.0489 | 0.0069 |
| 5-6 | | | | 0.0706 | 0.0339 |
| 3-8 | | | | 0.0770 | 0.0195 |
| 1-9(10,11) | | | | 0.0779 | 0.0027 |
| 1-3 | 0.0744(85) | 0.0748(85) | 0.0738(67) | 0.0665 | 0.0026 |
| 1-4 | 0.1108(109) | 0.1123(110) | 0.1128(93) | 0.1051 | 0.0022 |
| 1-5 | 0.1123(80) | 0.1107(79) | 0.1099(77) | 0.1089 | 0.0005 |
| 1-7 | 0.0584(34) | 0.0595(29) | 0.0569(39) | 0.0619 | 0.0028 |
| 2-4 | 0.0608(34) | 0.0619(29) | 0.0593(39) | 0.0645 | 0.0022 |
| 2-5 | 0.0749(60) | 0.0733(59) | 0.0762(67) | 0.0684 | 0.0021 |
| 3-5 | 0.0496(40) | 0.0492(38) | 0.0491(37) | 0.0605 | 0.0047 |
| 3-7 | 0.0594(34) | 0.0605(29) | 0.0579(39) | 0.0626 | 0.0039 |
| 4-7 | 0.0678(49) | 0.0667(48) | 0.0697(53) | 0.0649 | 0.0015 |
| 5-7 | 0.0893(44) | 0.0884(45) | 0.0889(43) | 0.0799 | 0.0005 |

the C_2-C_3 bond gave the value 0.5° with a standard deviation of 7° starting from the results of refinement C, thereby justifying our assumption of a planar heavy atom skeleton.

The value for the difference between C_1-C_2 and C_2-C_3 obtained in refinement C is of the order of three times its standard deviation. However, all the independent parameters could not be varied in this refinement and the difference is probably on the border of being significant.

The torsional angle $H_9C_1C_2C_3$ was included in the least-squares refinements to improve the agreement with the experimental data. This value should be interpreted as the single position best representing the thermal average of all the possible methyl group positions.

Then we regard the results of refinement C of Tables 1 and 2 as our final estimate of the structure. This result is also included in Fig. 4.

Several bond distances and bond angles have values as expected from related compounds. The C_1-C_2 (1.513 Å) and C_2-O_7 (1.212 Å) distances (R_α -values) agree quite well with the corresponding distances in acetone,²² 1.517 Å

Table 3. Atomic coordinates (Å) for pyruvaldehyde-1-oxime corresponding to the R_α -structure of refinement C of Table 1.

| Atom | x | y | z |
|------|---------|---------|---------|
| C1 | 0.0 | 0.0 | 0.0 |
| C2 | 0.0 | 1.5125 | 0.0 |
| C3 | 1.3016 | 2.2156 | 0.0 |
| N4 | 2.3801 | 1.5635 | 0.0 |
| O5 | 3.4901 | 2.3868 | 0.0 |
| H6 | 4.2365 | 1.7802 | 0.0 |
| O7 | -1.0133 | 2.1771 | 0.0 |
| H8 | 1.3909 | 3.2880 | 0.0 |
| H9 | 0.8193 | -0.3589 | -0.6030 |
| H10 | -0.9318 | -0.3589 | -0.4080 |
| H11 | 0.1125 | -0.3589 | 1.0110 |

and 1.211 Å, respectively (R_α -values). The N_4-O_5 (1.382 Å) and C_3-N_4 (1.260 Å) distances are somewhat shorter than those in formaldoxime,²³ found by microwave spectroscopy (1.408 Å and 1.276 Å, respectively). The length of the central C-C bond is consistent with a conjugated system and almost equals the one in acrolein.^{8,9} The angles $C_1C_2C_3$ and $O_7C_2C_3$ are equal (118.4°) which is surprising

because usually only the angle opposite to the double bond is smaller than 120° . The reason for this can be found in the steric interactions between the hydrogen atoms of the methyl group, the carbonyl oxygen atom and the C_3 atom.

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