

Measurements are available on the structure parameters for aromatic diacyl peroxides [1] and for araliphatic ones [2], but they are lacking for aliphatic ones.

We have examined the molecular geometry of the last by SCF MO LCAO in the MNDO approximation [3] for diacetyl peroxide (I), acetyl propionyl peroxide (II), and acetyl-2-methyl propionyl peroxide (III). In calculations on I, the bond lengths and angles were taken as identical in accordance with the C_2 symmetry. The rotations around the C-O bonds were taken as independent. For III, it was assumed that the CH_3 groups retain their tetrahedral structure. The geometrical parameters for both such groups in the hemmethyl moiety were taken as identical. In the optimization of II, no assumptions were made about symmetry retention in any of the parts. The calculations were compared with measurements via ones on the geometry on acetyl benzoyl peroxide (IV). A planar structure was assumed for the phenyl moiety, while all the other parameters were taken as independent.

A study of the rotation around the C-O bonds showed that there are potential-energy minima corresponding to the parallel and antiparallel A and B positions of the carbonyl bonds. For I, $\Delta E = E_A - E_B = 20.07$ kJ/mole, which corresponds to almost complete absence of the conformation state A at room temperature, in which one carbonyl bond is directed into the C-O-O-C dihedral angle, while the other is directed outwards. In B, the two bonds are directed inward. In case A, the dihedral angle is increased to 131.1° , while the calculated dipole moment rises to 5.06 D. The O-C-C bond angle is increased to 122.9° , which adjoins the C=O turned outward from the dihedral angle. The angle of emergence of this carbonyl bond from the C-O-O plane also alters. In the calculations on A, the optimization did not incorporate the symmetry conditions. We examined the rotation around the C-O bond adjoining only the methyl radical in III, since it is evident that rotation around the other C-O bond leads to even greater steric hindrance. The results were analogous to those for I. Such calculations were not performed for II, since the result is obvious.

Then we assume that I is in only one conformational state. Rotation of CH_3 around the C-C bond cannot lead to physically distinct conformation states because the hydrogen atoms in it are indistinguishable. Figure 1 shows calculated curves for the energy as a function of rotation angle $E = E(\varphi)$ for the substituent radicals for II and III, which have been calculated point by point, with φ fixed and all the other geometrical parameters optimized.

Molecule III has potential-energy minima for two angles of rotation of the hemmethyl group. One corresponds to the cis disposition of the C-H bond in the $CH(CH_3)_2$ group with respect to the C=O, where the calculated energy is -2195.99 eV ($\Delta H = -489.01$ kJ/mole). The other corresponds to trans positioning of C-H, and the energy is -2196.01 eV ($\Delta H = -490.98$ kJ/mole), which corresponds to a ratio of the populations of these states at room temperature of 1:2. The $E = E(\varphi)$ curve for II also has two minima, which correspond to almost perpendicular positioning of the O=C-C and C-C- CH_3 planes. In one case, the CH_3 group is directed toward the C-O-O-C dihedral angle, while in the other, it is directed away from it. These states are almost indistinguishable in energy.

The calculations for the parallel orientation of the carbonyl bonds show that one can get conformers related to rotation around the C-C bond.

MNDO applied to diacyl peroxides shows that the largest deviations in the calculated values from the measurements occur for the length of the O-O peroxide bonds, which is due to the choice of parameters [4]. The calculated dihedral angle between the C-O-O and O-O-C planes deviates from the observed one for IV because the calculation is for the isolated molecule, while the effects of the overall field should be quite pronounced, particularly for the dihedral angle.

Lenin Belorussian University. Translated from Zhurnal Strukturnoi Khimii, Vol. 28, No. 4, pp. 162-164, July-August, 1987. Original article submitted February 18, 1986.

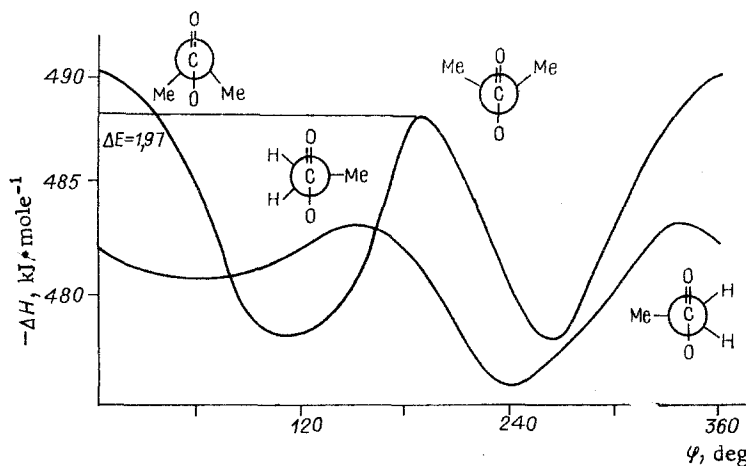


Fig. 1. Behavior of the energy for peroxides II and III as a function of angle of rotation of the substituent radical around the C-C α bond. The schemes near the minima are the Newman projections of the corresponding conformers along the C-C α bonds.

The peroxide group (peroxide core) C(O)OO(O)C in these diacyl peroxides is such that the atoms in the C-O-O-C chain are not coplanar. The calculations for the free molecule give a dihedral angle of 114°. The carbonyl bonds also do not lie in the C-O-O planes but are turned into the C-O-O-C angle in opposite senses. The angles of rotation are 6-7°. This disposition of the C=O bonds should mean that the IR spectra have the synphase (symmetrical) component of the doublet in the carbonyl absorption weaker than the antiphase (antisymmetric) one, as is observed. The structure of the C(O)OO(O)C groups in these aliphatic peroxides is in accordance with that in the aromatic and araliphatic peroxides, so change in the type of substituent has little effect on the conformation of the peroxide core. As the hydrogen atoms in the methyl moiety are replaced by CH₃ groups, one gets increases in the C-C α bond lengths (α is the position in relation to the corresponding carbonyl). The calculated rC-C α for I is 0.1523 nm, which becomes 0.1540 nm for III. The C α -CH₃ bond lengths in the aliphatic moieties vary similarly. The calculations also predict sequential lengthening of the C α -H bonds, whereas the rC-O remain almost identical for II and III, although being shortened by comparison with I.

These calculations show that in these aliphatic compounds the conformation changes have an effect on the geometrical parameters almost the same as that for increasing the length of the aliphatic substituent, which must be borne in mind in calculating normal vibrations for peroxides. It was found [5] that incorporating only the geometry changes for the different conformers does not always reproduce the features in the observed vibrational spectra, and it is necessary to examine the conservation of the force field to perform a more detailed comparison with experiment.

LITERATURE CITED

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