Ab initio study of the ground state and conformational stability of peroxyacetyl nitrate in internal rotation about the peroxide bond

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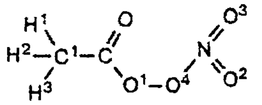
The molecular and electronic structure of the ground state of peroxyacetyl nitrate (PAN) was calculated by the unrestricted Hartree—Fock—Roothaan method with the use of the standard 3-21G and 6-31G basic sets. The potential curve of the internal rotation about the peroxide bond of PAN was calculated with the 6-31G basis set. The curve contains two maxima. The ground state of PAN is characterized by a structure in which groups of atoms adjacent to the peroxide bond lie in planes that are perpendicular to each other (the dihedral angle θ(COON) is 89.9°). The calculated barriers to rotation are 19.6 and 66.8 kJ mol^{-1}.

Key words: peroxyacetyl nitrate, *ab initio* quantum-chemical calculations, molecular structures, conformational analysis, barriers to internal rotation.

Peroxyacetyl nitrate (PAN) was first discovered in a photochemical smog atmosphere in Los Angeles.[1—3] It was established that PAN is formed as a result of photochemical oxidation of nonmethane hydrocarbons in the presence of nitrogen oxides according to the following reversible reaction:

$$\mathrm{MeC(O)OO^{\cdot} + NO_2^{\cdot} \rightleftharpoons MeC(O)OONO_2} \qquad (1)$$

and it is the most widespread representative of peroxy nitrates $\mathrm{XOONO_2}$, where X is the acyl or alkyl group. PAN was also detected in an ecologically pure atmosphere not only in the troposphere, but also in the lower stratosphere at concentrations comparable with those of nitrogen oxides.[1,4—17] PAN affects the formation of ozone in the troposphere through transfer of $\mathrm{NO_2^{\cdot}}$ and also provides additional generation of $\mathrm{MeC(O)OO^{\cdot}}$ and $\mathrm{NO_2^{\cdot}}$ radicals.



Because of the above-mentioned facts, PAN has attracted particular interest. However, its explosion hazard, toxicity, including mutagenic activity,[18] and thermal lability at room temperature impede its experimental studies, and its molecular structure has not been established yet. In this connection, *ab initio* quantum-chemical calculations that allow the determination of molecular structures of relatively small compounds containing atoms of light elements with an accuracy comparable with that obtained experimentally are of particular importance. Attempts to establish the geometry of the ground state of PAN, which we have made previously,[19—21] did not give an unambiguous answer to this question because of the conformational lability of the nitro and acyl groups relative to the peroxide bond.

Previously, the structure and conformational stability of peroxynitric acid, $\mathrm{HOONO_2}$ (PNA), have been studied.[22,23] It was demonstrated that, as in the case of hydrogen peroxide $\mathrm{H_2O_2}$, two minima and two maxima are present on the potential curve of the internal rotation about the peroxide bond. Moreover, it was found that the geometry of the ground state of PNA is such that the planes of the HOO and $\mathrm{NO_2}$ groups are almost perpendicular to each other. It is of interest not only to study PAN but also to compare the data on PAN with those on PNA and $\mathrm{H_2O_2}$. For this purpose, we calculated the geometry of the ground state of PAN and the potential curve of the internal rotation about the peroxide bond in the same approximation.

Calculation procedures

Calculations were carried out within the framework of the unrestricted Hartree—Fock—Roothaan method (UHF) using the GAUSSIAN-82 program on a CONVEX-C210 computer. The standard valence-split 3-21G and 6-31G basis sets were

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used. The molecular structure of the ground state of PAN was calculated with optimization of all geometric parameters in the UHF/3-21G and UHF/6-31G approximations. The potential curve of the internal rotation about the O(1)—O(4) bond was calculated by the UHF/6-31G method for the dihedral angle θ (CO(1)O(4)N), which was varied from 0 to 360° with a step of 10° (the remaining geometric parameters were optimized). The angles θ, which correspond to the minima and maxima of E_{tot} on this potential curve, were refined in the parabolic approximation using three points in the vicinity of the corresponding maximum or minimum. When the angle θ was estimated by this procedure, the remaining structural parameters were optimized in the same approximation (UHF/6-31G). The minimum on the potential curve that corresponded to θ = 89.9° was recalculated with full optimization of geometry. The calculations gave the values of E_{tot} and geometric parameters identical to the corresponding values, which were obtained for the angle θ estimated in the parabolic approximation.

Results and Discussion

The results of the calculations are given in Table 1. The bond lengths of the acyl group calculated in the UHF/3-21G and UHF/6-31G approximations differ by less than 0.01 Å. In the case of the O(1)—O(4) peroxide bond and the bonds in the nitro group, these differences are substantially larger. Thus, in going from the 3-21G to 6-31G basis set, the N—O(2) and O(1)—O(4) bond lengths decrease by 0.014 and 0.024 Å, respectively, and the shortening of the N—O(4) bond is maximum (0.047 Å). Previously, it has been demonstrated[23] that the geometric parameters of the ground state of PNA optimized in the UHF/6-31G, UHF/6-31G*, and MP2/6-31G* approximations agree qualitatively with each other. When the electronic correlation was taken into account by the MP2/6-31G method, the bond lengths of this molecule increase by ~3% compared to those obtained in the UHF/6-31G approximation. The exception is the N—O(4) bond the difference in the length of which is as large as 20%. It was noted[23] that the experimental N—O(4) bond length (1.50—1.53 Å), which was determined from the microwave spectra, is much closer to that calculated in the UHF/6-31G approximation (1.418 Å) than to the corresponding value calculated by the MP2/6-31G method (1.714 Å). Because both molecules, PAN and PNA, contain only

Table 1. Total energies (E_{tot}) and geometric parameters of PAN at different values of the CO(1)O(4)N angle (θ) calculated by the UHF method with the 6-31G and 3-21G basis sets

Parameter	6-31G				3-21G,
	0.0[a,b]	89.9[a,c]	179.9[a,b]	270.0[a,c]	84.0[a,d]
Bond			d/Å		
O(1)—O(4)	1.450	1.412	1.436	1.412	1.436
N—O(2)	1.197	1.199	1.200	1.202	1.213
N—O(3)	1.197	1.203	1.204	1.199	1.210
O(4)—N	1.456	1.425	1.408	1.425	1.472
C—O(1)	1.399	1.414	1.408	1.414	1.423
C(1)—C	1.490	1.488	1.492	1.488	1.495
O—C	1.194	1.191	1.191	1.191	1.183
H(1)—C(1)	1.081	1.082	1.081	1.082	1.083
H(2)—C(1)	1.081	1.081	1.082	1.082	1.082
H(3)—C(1)	1.078	1.078	1.078	1.078	1.078
Angle			φ/deg		
C—O(1)—O(4)	121.6	113.2	110.8	113.2	111.2
O(3)—N—O(2)	131.0	130.4	129.9	130.4	131.9
O(4)—N—O(3)	114.3	118.2	110.8	111.4	110.9
O(1)—O(4)—N	117.9	110.5	108.6	110.6	107.4
C(1)—C—O(1)	108.0	108.3	107.8	108.3	106.4
O—C—O(1)	122.8	121.8	122.9	121.8	122.1
H(1)—C(1)—C	110.2	109.9	110.2	110.1	109.2
H(2)—C(1)—C	110.0	110.2	110.2	110.0	109.8
H(3)—C(1)—C	108.5	108.8	108.6	108.8	109.1
O(4)—N—O(3)—O(2)	172.0	180.4	180.0	179.7	180.6
O(1)—O(4)—N—O(3)	92.9	188.7	180.0	171.2	187.3
C(1)—C—O(1)—O(4)	−179.5	−176.1	−179.6	−184.2	−179.4
O—C—O(1)—C(1)	180.0	180.3	179.9	179.8	180.1
H(1)—C(1)—C—O(1)	302.2	298.6	301.1	300.9	298.2
H(2)—C(1)—C—H(1)	119.2	119.1	119.2	119.1	118.6
H(3)—C(1)—C—H(1)	−120.5	−120.2	−120.4	−120.5	−120.4
			E_{tot} (au)		
	−505.67189	−505.69771	−505.69025	−505.69771	−503.11489

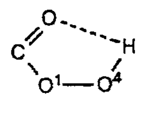
[a] θ/deg. [b] The maximum on the potential curve of the internal rotation. [c] The minimum on the potential curve of the internal rotation. [d] The ground state.

Period II atoms, it is believed that the use of the UHF/6-31G approximation for the optimization of geometry allows us to obtain sufficiently reliable data with moderate consumption of computer time for a large number of points of the calculated potential curve of the internal rotation.

Let us consider the changes in the angles for the ground state of PAN in going from the 3-21G to 6-31G basis set. The differences in the bond angles are no more than 1—2°, except for the O(1)O(4)N (3.1°) and O(4)NO(3) (7.3°) angles. The dihedral angles change by no more than 1°, except for the C(1)CO(1)O(4) (3.3°) and CO(1)O(4)N (5.5°) angles. Taking into account the above-mentioned accuracy of the UHF/6-31G approximation in the calculations of the geometry of PAN, it is evident that the 3-21G basis set is insufficient for this purpose. Hence, we discuss only the results obtained in the UHF/6-31G approximation.

The geometry of the ground state of PAN is characterized by the CO(1)O(4)N dihedral angle of 89.9°. Because the O(4)NO(3)O(2) angle is 180.4°, it can be assumed that these four atoms are in a single plane. The O(1) atom is also virtually in this plane ($\angle$O(1)O(4)NO(3) = 188.7°), whereas the C atom deviates from the plane so that θ = 89.9°. Therefore, the C—O(1) bond is perpendicular to the virtually planar O(4)NO(3)O(2) fragment. Taking into account that $\angle$C(1)CO(1)O(4) = −176.1° and $\angle$OCO(1)C(1) = 180.3°, it can be assumed that the O, C, O(1), and C(1) atoms are located in the vicinity of the plane that is virtually perpendicular to this fragment. The mutually perpendicular arrangement of the planes containing the groups that are adjacent to the O—O bond is attributable to the mutual repulsion of the lone electron pairs of the O atoms of the peroxide fragment and to the fixing of the position of the NO_2 group due to p—π conjugation. Therefore, an analogous mutual orientation of the planes of the fragments located on each side of the O—O bond would be expected in other peroxy nitrates.

Let us compare the calculated bond lengths and bond angles of PAN with the experimental data for the related compounds taking into account that PAN is a mixed anhydride of peroxyacetic and nitric acids[24—26] (Table 2). The experimental geometric parameters of MeC(O)OOH (**1**)[27] and $MeONO_2$ (**2**)[28] were determined from the microwave spectra. The experimental parameters of MeCOOH (**3**)[29] were obtained by electron diffraction study. The experimental data for crystalline diacetyl peroxide (**4**),[30,31] glycerol trinitrate (**5**),[32] and acetyl benzoyl peroxide (**6**)[33] were determined by X-ray diffraction analysis. On the whole, the calculated and experimental values of the bond lengths and bond angles of the structurally similar groups are in close agreement (see Table 2). Thus, the $CONO_2$ fragment in methyl nitrate[2] is planar, which corresponds to the CONO dihedral angle of 180°. Analogously, the values of the O(1)O(4)NO(3) angle in PAN at the minima of the potential curve of the internal rotation are 188.7 and 171.2°. The XOOY dihedral angle is 84.9° and 86.6° in molecules **4** and **6**, respectively, whereas in molecule **1**, all atoms are virtually in a single plane due to fixation of the ring through a hydrogen bond.[30,31]



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In addition to two minima, which correspond to the ground state of PAN, the potential curve of the internal rotation (Fig. 1) has two maxima. As can be seen from Table 1, in the region of the maxima on the potential curve the CO(1)O(4)N dihedral angle takes the values 0 and ~180°. Let us consider the geometry of the PAN molecule at each of these maxima. At the first of them ($\angle$CO(1)O(4)N = 0°), the O(4)NO(3)O(2) and $\angle$O(1)O(4)NO(3) dihedral angles are 172.0 and 92.9°, respectively, *i.e.*, the O(4)NO(3)O(2) fragment is virtually planar, and the O(1)—O(4) bond is perpendicular to this fragment. Unlike the first maximum, the second one (θ = − 179.9°) is characterized by the location of all atoms of the PAN molecule, except for H atoms, in a single plane ($\angle$C(1)CO(1)O(4) = 179.5°). As is seen from Table 1, the first and the second maxima are characterized by the barriers to rotation 66.8 and 19.6 kJ mol^{-1}, respectively.

Table 2. The bond lengths (*d*) and bond angles (φ) of the ground state of PAN calculated by the UHF/6-31G method and the experimental parameters of the related compounds (**1**—**6**)

Parameter	Calculation for PAN	Experimental data
Bond	*d*/Å	
N=O(2)	1.199	1.205 (*cis*-**2**); 1.198—1.200[a] (*cis*-**5**)
N=O(3)	1.203	1.208 (*trans*-**3**); 1.199—1.204[a] (*trans*-**5**)
O(4)N	1.425	1.402 (**2**); 1.402—1.414[a] (**5**)
C—O(1)	1.414	1.33 (**1**); 1.361 (**3**); 1.371 (**6**)
C(1)—C	1.488	1.49 (**1**); 1.517 (**3**); 1.388 (**4**); 1.485 (**6**)
C=O	1.191	1.22 (**1**); 1.212 (**3**); 1.187 (**6**)
H(1)—C(1)	1.082	1.09 (**1**); 1.100 (**3**)
H(2)—C(1)	1.081	1.09 (**1**); 1.100 (**3**)
H(3)—C(1)	1.078	1.09 (**1**); 1.100 (**3**)
O(1)—O(4)	1.412	1.47(**1**); 1.455 (**4**); 1.445 (**6**)
Angle	φ/deg	
C—O(1)—O(4)	113.2	112.9 (**1**); 110.8 (**4**); 111.2 (**6**)
O(3)=N=O(2)	130.4	129.5 (**2**); 129.5—129.9[a] (**5**)
O(4)—N=O(3)	118.2	116.5 (*cis*-**2**); 112.4 (*trans*-**2**); 118.1—118.5 (*cis*-**5**); 111.8—112.0 (*trans*-**5**)
O(1)—O(4)—N	110.5	96.6[b] (**1**); 112.7[c] (**2**)
C(1)—C—O(1)	108.3	110.0 (**1**); 110.6 (**3**); 108.0 (**6**)
O=C—O(1)	121.8	123.0 (**3**); 123.3 (**6**)
H(1)—C(1)—C	109.9	108.8 (**1**)
H(2)—C(1)—C	110.2	108.8 (**1**)
H(3)—C(1)—C	108.8	108.8 (**1**)

[a] The limits of the values in the three ONO_2 groups of molecule **5**. [b] The O—O—H angle in molecule **1**. [c] The O—O—N angle in molecule **2**.

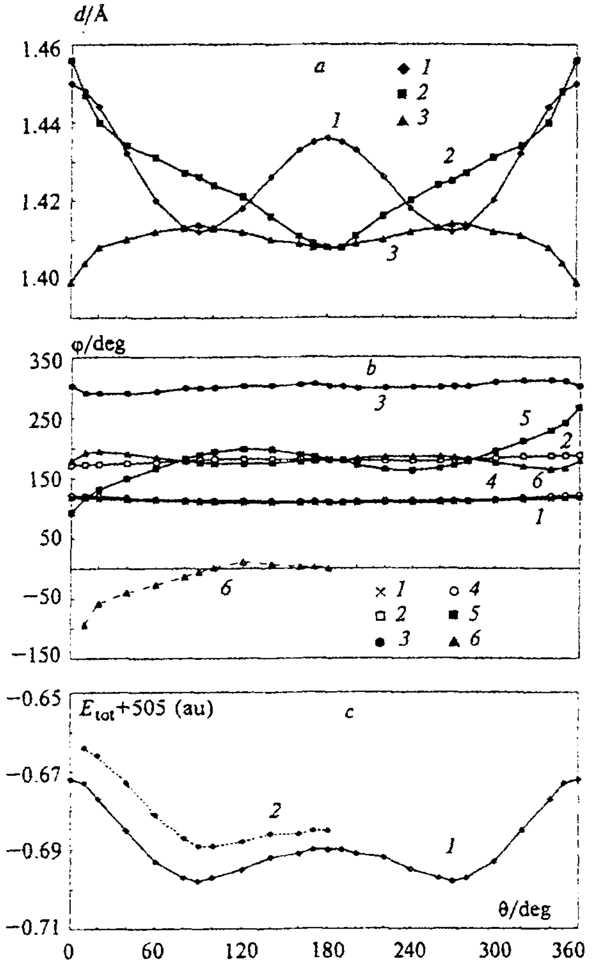


Fig. 1. Dependence of (*a*) the O(1)—O(4), N—O(4) (*2*), and C—O(1) (*3*) bond lengths (*d*), (*b*) the O(1)O(4)N (*1*), O(4)NO(3)O(2) (*2*), H(1)C(1)CO(1) (*3*), CO(1)O(4) (*4*), O(1)O(4)NO(3) (*5*), and C(1)CO(1)O(4) (*6*) angles (φ), and (*c*) the total energy E_{tot} in the case of the *trans* (*1*) and *cis* (*2*) positions of the C(1) and O(4) atoms of the peroxyacetyl nitrate molecule on the dihedral angle θ(CO(1)O(4)N).

According to the calculations,[22] the barriers to internal rotation about the O—O bond in PNA increase by only 2—4 kJ mol^{-1} in going from the UHF/6-31G to MP4/6-31G* approximation. Because both molecules, PAN and PNA, consist of Period II elements and hydrogen, and in the regions of the maxima and minima the orientation of the groups adjacent to the peroxide bond are similar, it is reasonable to suppose that account of the correlation energy in the case of PAN results in a change in the barriers by no more than 4—5 kJ mol^{-1}. The curves in Fig. 1 allow one to characterize in detail the changes in the geometric parameters of the PAN molecule as the angle θ increases from 0° to 360°.

Only three bonds (O(1)—O(4), N—O(4), and C—O(1)) change substantially when moving along the potential curve of the internal rotation. The differences in the bond lengths of the methyl group are no more than 0.001 Å. The changes in the C—O, C(1)—C, N—O(2), and N—O(3) bond lengths are no more than 0.007 Å. The changes in the O(1)—O(4), N—O(4), and C—O(1) bond lengths are symmetrical with respect to θ = 180°. The C—O(1) bond has the maximum and minimum lengths in the regions of the minima and maxima of the potential curve, respectively. Unlike the C—O(1) bond, the O(1)—O(4) and N—O(4) bonds are most elongated in the region of the higher barrier (θ = 0° (360°)). However, the O(1)—O(4) and N—O(4) bonds differ in that the N—O(4) bond length decreases monotonically as the angle θ changes from 0 to 180°, while the O(1)—O(4) bond length first decreases as the angle θ changes from 0 to 90° and then increases as θ changes from 90 to 180°. Apparently, this behavior of the O(1)—O(4) and N—O(4) bonds is determined by the fact that (as the analysis of the changes in the dihedral angles when moving along the potential curve demonstrated) two complete revolutions about the O(1)—O(4) bond are accompanied by only one complete revolution about the N—O(4) bond. In this case, the N—O(4) bond is elongated owing only to the mutual repulsion between the acetyl and nitro groups, which is maximum in the *cis* form, while the O—O bond is elongated additionally due to the mutual repulsion of the p-orbitals of the O(1) and O(4) atoms, which is maximum in the *cis* and *trans* positions of the C and N atoms with respect to the peroxide bond (θ = 0° and 180°). Therefore, the O(4)NO(3)O(2) nitro group behaves as a rather rigid fragment, which suggests the presence of strong bonding in its π system. Similarly, the mutual arrangement of the atoms of the methyl group remains virtually unchanged. Thus, when the deviation of the H(1)C(1)CO(1) angle from ~302° along the potential curve is maximum (±10°), the H(2)C(1)CH(1) and H(3)C(1)CH(1) angles change by no more than 1°, and the H_i—C(1) bond lengths (i = 1—3) remain virtually unchanged.

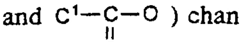
Table 3. Effective charges on the atoms of PAN (according to Mulliken) at different values of the C—O(1)—O(4)—N angles (θ)

Atom	Effective charge/e			
	0.00[a,b]	89.9[a,c]	179.9[a,b]	270.0[a,c]
O(2)	−0.280	−0.302	−0.312	−0.333
N	0.613	0.708	0.729	0.709
O(3)	−0.279	−0.334	−0.319	−0.304
O(4)	−0.114	−0.149	−0.184	−0.149
O(1)	−0.368	−0.364	−0.380	−0.363
C	0.742	0.750	0.765	0.750
C(1)	−0.524	−0.533	−0.530	−0.533
O	−0.492	−0.471	−0.465	−0.472
H(1)	0.234	0.235	0.231	0.230
H(2)	0.234	0.229	0.231	0.235
H(3)	0.234	0.231	0.230	0.231

[a] θ/deg. [b] The maximum on the potential curve of the internal rotation. [c] The minimum on the potential curve of the internal rotation.

As in the case of PNA,[22] the barriers to internal rotation and the shape of the potential curve for PAN are affected by the interaction of the p-orbitals of the peroxide O atoms and by effective charges on the other atoms. The effective Mulliken charges for the structures that correspond to the maxima and minima on the potential curve are given in Table 3. The most substantial redistribution of the charges in the molecule is observed on the O(2), O(3), O(4), and N atoms in the region of the absolute maximum on the potential curve, which is characterized by ∠CO(1)O(4)N = 0°.

The shape of the potential curve of the internal rotation is similar to that observed in the case of the HOOH molecule,[30,31] namely, the minima at $\theta = 89.9°$ and 270° are identical, the higher barrier (68 kJ $\mathrm{mol^{-1}}$) corresponds to the *cis* arrangement ($\theta = 0°$) of the C and N atoms with respect to the peroxide bond, and the lower barrier (19.6 kJ $\mathrm{mol^{-1}}$) corresponds to their *trans* arrangement ($\theta = 179.9°$). The calculated routes of transitions from one rotational conformer to the other correspond to the minimum barriers to rotation. The theory of the transition state assumes the possibility of multichannel reactions,[34] *i.e.*, of several routes of transitions from the initial compounds to the final products. Hindered rotation about the O—O bond in PAN can also occur through different channels on the multidimensional potential energy surface due to the presence of several groups, which can rotate with respect to each other.

When rotated about the O(1)—O(4) peroxide bond, the C(1) and O(4) atoms can occur both in the *cis* and *trans* positions with respect to the C—O(1) bond, while the mutual arrangement of the atoms of the remaining fragments ($\mathrm{ONO_2}$ and  $\mathrm{C^1{-}\underset{\underset{O}{\|}}{C}{-}O}$) changes only slightly when moving along the potential curve, which corresponds to the known concepts of their molecular structures. Let us compare the characteristics of the internal rotation calculated for these two states of PAN in the UHF/6-31G approximation, where the angle θ was varied from 180 to 0° with a step of 10° starting from the *cis* arrangement of the C(1) and O(4) atoms (∠C(1)CO(1)O(4) = 0°) followed by optimization of the remaining structural parameters (including ∠C(1)CO(1)O(4)). In Fig. 1, the calculated potential curve of the internal rotation and the corresponding dependence of ∠C(1)CO(1)O(4) on θ are shown by dashed lines.

As is seen from Fig. 1, the values of ∠C(1)CO(1)O(4) are in the ~0—11° range as θ decreases from 180 to 90°, and as θ decreases from 90 to 10°, the value of ∠C(1)CO(1)O(4) varies from ~5 to ~93°, *i.e.*, $\theta \approx 10°$, apparently, corresponds to the beginning of transition of the C(1) and O(4) atoms from the *cis* to the *trans* position with respect to the C—O(1) bond. (For the values of θ in the 10—0° range, the iterative procedure does not converge). The potential curve of the internal rotation, which was calculated according to this procedure, lies 12—30 kJ $\mathrm{mol^{-1}}$ above the curve that corresponds to the *trans* arrangement of the C(1) and O(4) atoms ($\Delta E \approx$ 12—20 kJ $\mathrm{mol^{-1}}$ as θ decreases from 180 to 90°, and $\Delta E \approx$ 20—30 kJ $\mathrm{mol^{-1}}$ for θ in the range from 90 to 0°). For ∠C(1)CO(1)O(4) ≈ 0°, the potential curve that corresponds to the *cis* arrangement of the C(1) and O(4) atoms is sharply elevated (see Fig. 1, *c*, curve *2*), which indicates that further rotation about the O—O bond is impossible due to steric hindrances caused by the atoms of the methyl and nitro groups.

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