

THE PHOTOELECTRON SPECTRA OF ALKYLPEROXIDES^[1]

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Photoelectron spectroscopic investigations of lone pair-lone pair interactions have been reported for hydrazines (1)^[2] and for disulfides (2)^[3]. In this note the corresponding data for peroxides are presented *i.e.* *tert*-butylhydroperoxide (5), di-*tert*-butylperoxide (6), 3,3,5,5-tetramethyl-1,2-dioxolane (7), and 3,3,6,6-tetramethyl-1,2-dioxane (8) (see Figure 1 and Table 1).

Band	5; $\theta \approx 90^\circ$	6; $\theta \approx 180^\circ(?)$	7; $\theta = 0^\circ$	8; $\theta = 90^\circ$
①	10.2 ₄ a(π^-)	8.7 ₈ 1b _g (π^-)	9.2 ₅ 1a ₂ (π^-)	9.5 ₅ a(π^-)
②	10.2 ₄ b	10.4 ₆ 4a _g	10.4 ₀ 3b ₁	9.5 ₅ b
③	11.3 ₃ a	10.8 ₅ 1a _u	11.4 } 4a ₁	10.9 a
④	12.3	11.7	11.8 } or 1b ₂	11.7

Table 1. PES (vertical) ionization potentials for 5, 6, 7 and 8. Orbital labels refer to corresponding orbitals in 3. Values in eV.

MINDO/2 molecular orbital calculations^[4] indicate that the conformational dependence of the energies for the five highest occupied orbitals of H₂O₂ (3) on the dihedral angle θ is qualitatively as shown in Figure 2 ($\theta = 0^\circ$: *s-cis*-conformation, symmetry C_{2v}; $\theta = 180^\circ$: *s-trans*-conformation, symmetry C_{2h}). This is supported by more sophisticated calculations^[5,6] which also discuss the rotational barrier of 3. (See however the results of ref. [7] for a slightly different assignment.) Extended Hückel (EH) calculations^[8] again yield about the same result. Apart from small changes which are due to differences in basis orbital energies and in their interaction matrix elements, the sequence and

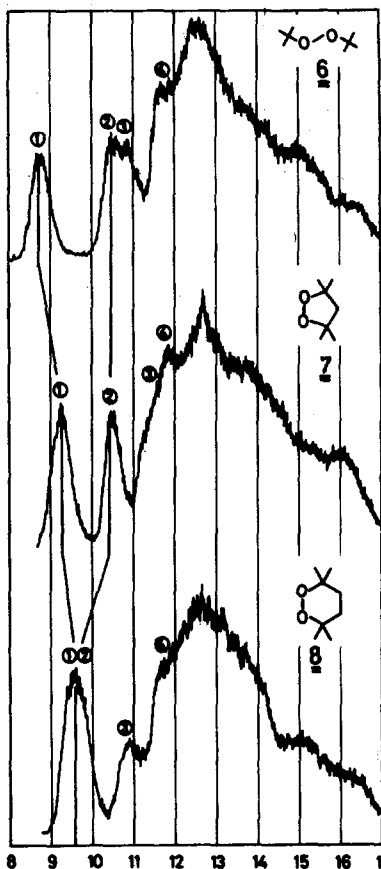


Figure 1: HeI Photoelectron Spectra of 6, 7 and 8.

trends shown in Figure 2 for 3 are about the same as found by Wagner and Bock for 2^[3] (cf. Figure 4 of their paper for a graphical representation of the molecular orbitals as a function of θ).

In the molecules 1, the two highest occupied orbitals are essentially the out-of-phase and the in-phase linear combinations of the nitrogen lone-pair orbitals. In contrast, the highest occupied orbitals $1a_2(C_{2v})$ and $1b_g(C_{2h})$ of 3 are the out-of-phase combination $(2p_a - 2p_b)/\sqrt{2}$ of the oxygen $2p_x$ atomic orbitals, and the second highest orbital $3b_1(C_{2v})$ and $4a_g(C_{2h})$ is best described as a linear combination $(\phi_{OH,a} - \phi_{OH,b})/\sqrt{2}$ of the OH σ -bond orbitals. In the range $0 < \theta < 180^\circ$, σ/π separation breaks down (i.e. $1a_2(\pi) \rightarrow 5a + 4a_g$; $3b_1 + 4b + 1b_g(\pi)$) and the mixed orbitals 5a and 4b (symmetry C_2) become accidentally degenerate near $\theta = 90^\circ$. For simplicity we keep the orbital designations of 3 for the derivatives 4 to 8.

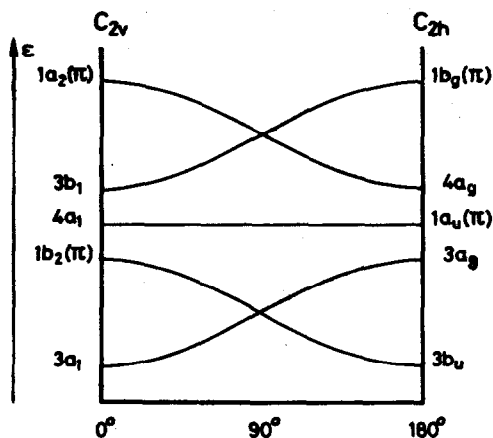
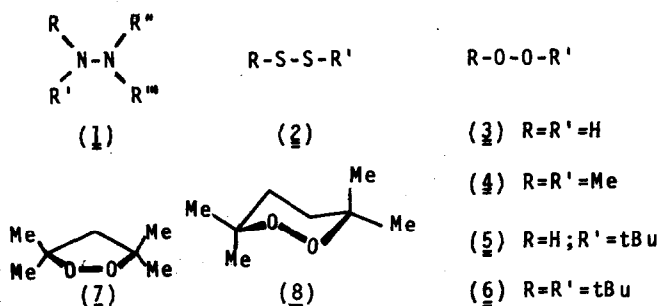


Figure 2: Qualitative orbital correlation diagram for 3 as a function of θ



In Table 2 some theoretical results for 3 and 4 are summarized.

Table 2. Calculated orbital energy differences (Δ) for the two highest occupied MO's of 3 and 4 according to MINDO/2 and EH methods.

	0°	30°	60°	90°	120°	150°	180°	
Δ : <u>3</u>	1.13	1.00	0.62	0.16	-0.26	-0.57	-0.69	MINDO/2
<u>4</u>	1.18	0.73	0.03	-0.21	-0.51	-0.84	-1.00	MINDO/2
<u>3</u>	1.25	0.98	0.54	0.07	-0.39	-0.74	-0.88	EH

From the data shown in Table 2 one can see that Methyl substitution of 3 (to yield 4 under the assumption of zero change in length $r_{00} = 1.475 \text{ \AA}$ [9] and a small change in bond angle $\alpha_{00H} = 94.8^\circ$ [9], $\alpha_{00C} = 110^\circ$ (assumed) has no marked influence on the size and the θ -dependence of the split $\Delta = \epsilon(5a) - \epsilon(4b)$.

The calculations also show that the mean orbital energy $\bar{\epsilon} = (\epsilon(5a) + \epsilon(4b))/2$ is practically independent of θ , decreasing only by 0.2₅ to 0.3₅ eV from $\theta = 0^\circ$ to 180°.

We shall assume that these observations can be applied in a first approximation to 6, 7 or 8. This is not really true but our sample is much too small to allow a discrimination between the different parameters which must necessarily enter into a more detailed discussion of Δ and $\bar{\epsilon}$.

Models suggest that $\theta = 0^\circ$ in 7 and $\theta = 80^\circ$ to 90° in 8. From the data in Table 2 we expect $\Delta_{\text{calc}}(\underline{7}) = 1.0$ to 1.2 eV and $\Delta_{\text{calc}}(\underline{8}) = 0$ eV in agreement with the data collected in Table 1 (applying Koopmans' approximation [10]). The lower value $\bar{\epsilon}(\underline{8}) = 9.5_5$ eV relative to $\bar{\epsilon}(\underline{7}) = 9.8_0$ eV can be explained as a consequence of the larger size of the alkyl moiety.

Dipole moment measurements in solution [11] yield $\theta = 100^\circ$ for 5 and $\theta = 123^\circ$ for 6

(cf. $\theta = 111^\circ$ for 3 in the gas phase [9]). Our PE spectrum for 5 is compatible with the θ value given above, although the loss in symmetry due to monosubstitution which forbids orbital crossings makes it difficult to apply the observations embodied in the data of Table 2. For 6, two bands separated by $\Delta = 1.8$ eV are observed which could be interpreted as indicating a value θ near 180° . The integrated intensity and the half width of band (1) make it seem improbable that this first band at 8.8 eV is due to two overlapping bands. Thus we believe that 6 exists in the vicinity of the *s-trans*-conformation in the gas phase.

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