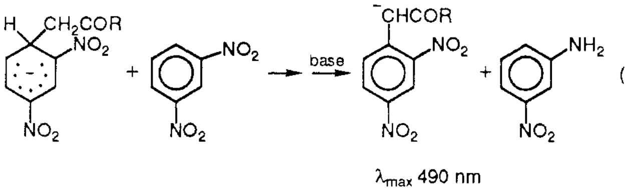
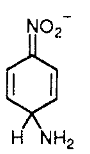
for the photooxidations of **11**, **16**, and **17**. These species are NADH analogues,[34] and a kinetic isotope effect (k_H/k_D) of 5 has been reported[35] for a thermal oxidation of one such species.

These findings shed light on several mysteries of nucleophilic aromatic photosubstitutions involving the displacement of hydrogen. The stability of neutral **11** and anionic **16** and **17** toward oxygen is surprising in view of the frequent observation[1-3,5-8] that oxygen must be present in order to form aromatized products. Structural differences may account for this difference. Moreover, at the high concentrations of preparative photoreactions,[1-3,5-8] oxygen may participate in radical chain reactions that are photoinitiated; such reactions may not occur efficiently at the lower substrate concentration we have used. Our observation that 3,5-dinitrobenzoate ion is a sufficiently strong acceptor to oxidize **11**, **16**, and **17** can be correlated with the known success of the Zimmermann reaction, a color test for enolizable ketones that depends on the thermal oxidation of a Janovsky complex by a dinitrobenzene (eq 3).[36]



(3)

On the basis of our findings for **16** and **17**, we suggest that the oxygen-stable intermediate (λ_{max} 335 nm) observed when nitrobenzene is photolyzed in liquid ammonia[1] is **24** rather than the proposed structure **25**. Anion **24** in a polar protic solvent could well absorb at 335 nm whereas **25** would be little different in its UV spectrum from anilinium ion (λ_{max} 254 nm).[37]



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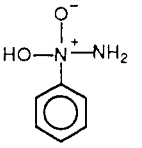

25

Experimental Section

D_2O and 30% NaOD in D_2O were 99.8% deuterium from Aldrich. **1** was available from a previous study.[11] NMR spectra were obtained with an IBM/Bruker NR/300 spectrometer with samples in 5-mm tubes at 25 °C. Proposed couplings were all verified by spin decoupling experiments. UV spectra were obtained with a Beckman 5260 spectrophotometer with samples in 1.00-cm quartz cuvettes.

Samples were prepared in volumetric flasks at 0 °C by weighing and quantitative transfer with syringes. Irradiations were carried out at 0 °C in a Rayonet RPR-208 reactor with 350-nm lamps. NMR sample tubes were suspended in the reactor in an Ace Glass jacketed quartz well maintained at 0 °C by circulating ethanol–water coolant. Terephthalic acid (as its dianion, δ 7.86) was used as an internal standard for the NMR spectra.

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Registry No. 1, 60814-16-6; 1-*N,N*-d_2, 123934-49-6; 2-*N*-*d*, 123934-50-9; 3-*N,O*-d_2·Na, 123934-51-0; 6-*N,O*-d_2, 123934-52-1; A, 123962-98-1; B·Na, 123962-99-2; C·Na, 123934-53-2.

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Electronic Structure of [*n*.1.1]Propellanes. PE Spectroscopic Investigations

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The PE spectra of five [*n*.1.1]propellanes have been recorded. The first four PE bands have been assigned by comparison with bicyclobutane derivatives and by comparison with the results of MINDO/3 and ab initio (STO-3G) calculations. We find that the energy of the first band depends very strongly on *n*. For $n = 1$ the ionization energy is located around 9 eV, for $n = 3$ and 4 it is recorded above 8 eV. This difference is ascribed to two effects, the inductive effect of the methylene groups and the lower s character for $n = 3$ and 4 as compared to $n = 1$.

Among the [*m.n.o*]propellanes[1] the most interesting examples are the ones that are highly strained [$m, n, o < 3$). The recent synthesis of [1.1.1]propellane **1**[2] and several of its congeners[3-5] provided the motivation of our study concerning the electronic structure of strained propellanes. In 1972 two groups investigated the electronic structure of **1**[6,7] using the extended Hückel method and a Hartree–

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Table I. Comparison between the Recorded Vertical Ionization Energies, $I_{v,j}$, and the Calculated Orbital Energies, ϵ_j, of 2–6 (All Values in eV)

compd	band	$I_{v,j}$	assignmt	$-\epsilon_j$(MINDO/3)	$-\epsilon_j$(STO-3G)
2	1	7.8	$12a_1$	8.21	6.57
	2	9.6	$4a_2$	9.59	8.71
	3	9.8	$7b_2$	9.72	9.31
	4	10.1	$7b_1$	10.34	10.11
3	1	7.78	$11a_1$	8.06	6.36
	2	9.6	$3a_2$	9.76	9.21
	3	9.9	$6b_1$	10.35	10.27
	4	10.3	$7b_2$	10.28	10.67
4	1	9.35	$9a_1$	9.21	7.59
	2	10.4	$2a_2$	9.64	9.47
	3	10.7	$4b_1$	10.00	10.00
	4	11.2	$6b_2$	10.22	11.20
5	1	7.86	$10a_1$	8.10	6.57
	2	9.7	$3a_2$	9.48	8.77
	3	10.0	$5b_1$	10.56	11.19
	4	10.4	$6b_2$	10.60	11.02
6	1	9.56	$8a_1$	9.16	7.65
	2	10.3	$2a_2$	9.38	9.10
	3	11.2	$3b_1$	10.22	10.63
	4	11.9	$5b_2$	10.60	11.99

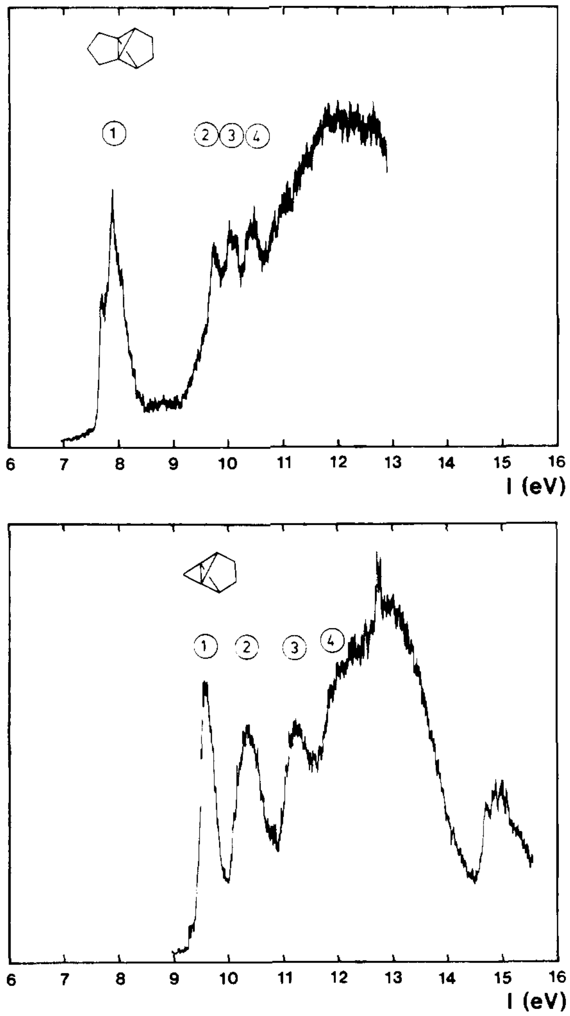

Figure 1. He(I) PE spectra of **5** and **6**.

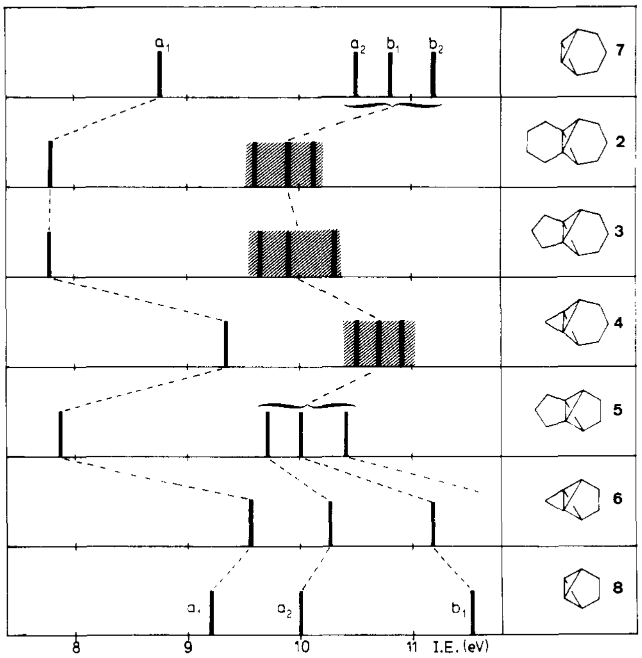

Figure 2. Correlation diagram between the first bands in the PE spectra of **2**–**8**.

Fock SCF procedure with a 4-31G basis.[8] Spurred by the synthetic success several calculations on propellanes have appeared more recently.[9] A recent study concerning the bond between the bridgeheads[9c] predicts a more spread out charge density than usual. Furthermore the MO calculations show that the HOMO of **1** is slightly antibonding and can best be described by an $sp^{4.5}$ hybridized carbon atom pointing outward from each bridgehead position.[9l] It is interesting to compare these predictions with experimental results. High resolution X-ray studies on **4**, **6**,[10] and a [3.1.1]propellane derivative[11] yield a diffuse positive difference density at each inverted C atom, outside the bridgehead bond, and a slightly negative difference density between the bridgeheads. This latter finding might be due to the choice of the spherical atom reference state.[12] The PE investigations on **1**[13] reveal that there should be only minute changes in geometry between **1** and its radical cation. This can be attributed to the nonbonding or slightly antibonding character of the HOMO of **1** ($5a_1$). A PE investigation on a less strained [3.1.1]propellane[14] is

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indicative for a slightly bonding HOMO.

To contribute to the discussion of the electronic structure of highly strained propellanes, we have investigated the He(I) photoelectron (PE) spectra of tetracyclo-[5.4.0.0^{1,6}.0^{2,7}]undecane (**2**), tetracyclo[5.3.0.0^{1,6}.0^{2,7}]decane (**3**), tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane (**4**), tetracyclo-[4.3.0.0^{1,5}.0^{2,6}]nonane (**5**), and tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptane (**6**).


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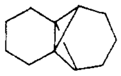
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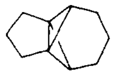
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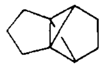
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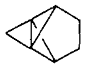
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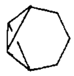
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8

Results

The PE spectra of **5** and **6** in Figure 1 are typical examples of this class of compounds. The recorded first ionization energies of **2**–**6** are collected in Table I. Common to all spectra is a relatively sharp peak at low energy well separated from strongly overlapping features. To interpret the spectra we have correlated the first bands of **2**–**6** with the bands of tricyclo[4.1.0.0^{2,7}]heptane (**7**) and tricyclo[3.1.0.0^{2,6}]hexane (**8**) whose PE spectra have been reported earlier.[15,16] In Figure 2 the corresponding diagram is shown. The comparison between the first PE bands of **7** with those of **2** and **3** reveal a shift of all bands toward lower energy by about 1 eV. We ascribe this shift to the inductive effect of the tetramethylene bridge. Similarly we observe a strong shift when comparing the first band of **8** with that of **5**. The correlation made in Figure 2 also suggests assignment of at least three bands arising from a_2, b_1, and b_2 MO's to the broad peak between 9 and 11 eV in the PE spectra of **2**–**6**.

Comparison between the first band of the PE spectra of **4** and **6** with that of the corresponding bicyclobutane derivatives **7** and **8** shows shifts toward higher energy by 0.4 and 0.6 eV, respectively. A similar shift (0.35 eV) toward higher energy is encountered when comparing the first PE band of **1**[13] with that of bicyclobutane.[16] We ascribe this high energy shift to two opposing effects: the inductive effect of the CH_2 group, which induces a shift toward lower energy, and the higher s character of the corresponding HOMO of the propellane as compared to the bicyclobutane derivative. In the latter compound the HOMO is predicted to be mainly of 2p character.[16,17] To estimate roughly the inductive effect of the CH_2 group on the HOMO of **1**, we have compared the first PE band of *n*-pentane (10.93 eV)[18] with that of *n*-butane (11.09 eV).[18] This comparison suggests to use at most 0.2 eV for the inductive effect of a CH_2 group in **1**, **4**, and **6**. A similar value is obtained when comparing the first PE band of bicyclo[1.1.1]pentane (10.6 eV)[19] with that of cyclobutane (10.7 eV).[20] Thus the increase of the ionization energy that is due to the higher 2s character in the HOMO amounts approximately to 0.5 eV.

To check our empirical assignments and our arguments with respect to the nature of the highest occupied molecular orbitals of **2**–**6**, we have carried out MO calculations on these molecules. The methods applied were the HF-SCF procedure with a STO 3G[8] basis and the MINDO/3 method.[21] The latter procedure was also used to calculate the geometrical parameters of **2**–**6**. The comparison between the calculated orbital energies and the recorded ionization energies (see Table I) is based on the assumption that Koopmans' theorem[22] is valid. From Table I it is seen that the values derived by the MINDO/3 method agree very well with experiment. The HOMO (a_1) is predicted to be well separated from three close lying MO's belonging to the irreducible representations A_2, B_1, and B_2. The sequence of these latter MO's depends on the molecule and on the method used (see Table I). The large changes between **2**, **3**, and **5** on one side and **4** and **6** on the other are reproduced well.

The amount of s character predicted in the HOMO for **2**, **3**, and **5** varies between 1.2–2.1% (MINDO/3) and 1.2–3.5% (STO-3G). The s character for **4** (12.2% (MINDO/3), 19.3% (STO-3G)) and **6** (12.2% (MINDO/3), 19.3% (STO-3G)) is predicted to be considerably higher. Thus the calculations corroborate our interpretation that the strong changes in the first ionization energy between the [*n*.1.1]propellanes with $n > 1$ and those with $n = 1$ are mainly due to the difference in s character and partly due to the change in the inductive effect of the bridging moiety.

Experimental Section

The preparation of the propellanes **3**,[23] **4**,[4,5b] and **6**[4,5b] has been described in the literature. Compounds **2**[24] and **5**[25] were synthesized in analogy to **3**. All compounds were prepared shortly before the PE measurement. The PE spectra were recorded on a PS 18 photoelectron spectrometer equipped with a He(I) source (Perkin Elmer Ltd., Beaconsfield). The spectra were calibrated with argon and xenon, and a resolution of about 20 meV on the argon line was obtained.

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