**Scheme I**[a]

(m, 1 H), 2.64 (br d, $J$ = 11 Hz, 1 H), 3.02 (s, 3 H, CH$_3$SO$_3$), 4.06 (dd, $J$ = 9, 10 Hz, 1 H), 4.42 (dd, $J$ = 4.5, 10 Hz, 1 H), 5.56 (m, 1 H), 5.92 (d, $J$ = 15.5 Hz, 1 H), 6.86 (dd, $J$ = 11, 15.5 Hz, 1 H); $^{13}$C NMR (25 MHz, CDCl$_3$) δ 17.1 (q), 22.7 (q), 26.3 (t), 26.7 (q), 34.9 (s), 37.2 (q), 42.9 (d), 55.3 (d), 71.0 (t), 121.6 (d), 124.6 (d), 131.9 (s), 151.2 (d), 170.9 (s); MS (70 eV) $m/z$ 206 (6), 138 (25), 93 (100), 79 (17), 41 (18). Anal. Calcd for C$_{14}$H$_{22}$O$_5$S: C, 55.61; H, 7.33; S, 10.60. Found: C, 55.58; H, 7.29; S, 10.66.

*cis*(1′,5′)-(2E)-3-(2′,5′,6′,6′-Tetramethyl-2′-cyclohexen-1′-yl)-2-propenoic Acid (10). A mixture of mesylate 9 (303 mg, 1 mmol), sodium iodide (600 mg, 4 mmol), zinc (520 mg, 8 mmol, powder), and 6 mL of dimethoxyethane was heated in an oil bath at 90 °C for 4 h. After cooling, the reaction mixture was filtered through Celite and the flask rinsed with ether and water. The combined filtrates were acidified with dilute hydrochloric acid and extracted with ether (2 × 150 mL). The organic extracts were dried (MgSO$_4$), filtered, and concentrated in vacuo. Filtration through a pad of silica gel (5 g) with pentane/ether (1:1) as eluent afforded 158 mg (76%) crystalline 10. An analytical sample was prepared by recrystallization from pentane at −30 °C: mp 115–116 °C; IR (CHCl$_3$) 3500–2500 (br), 1695, 1645 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.71 (s, 3 H), 0.86 (d, $J$ = 7 Hz, 3 H), 0.87 (s, 3 H), 1.42–1.52 (m, 1 H), 1.53 (m, 3 H), 1.68–1.81 (m, 1 H), 1.89–1.99 (m, 1 H), 2.59 (br d, $J$ = 11 Hz, 1 H), 5.51 (m, 1 H), 5.89 (d, $J$ = 15.5 Hz, 1 H), 6.95 (dd, $J$ = 11, 15.5 Hz, 1 H); $^{13}$C NMR (25 MHz, CDCl$_3$) δ 15.1 (q), 15.4 (q), 22.7 (q), 26.7 (q), 32.0 (t), 35.9 (s), 38.1 (d), 56.0 (d), 123.0 (d), 123.9 (d), 131.8 (s), 152.9 (d), 171.6 (s); MS (70 eV) $m/z$ 208 (6, M$^+$), 138 (41), 123 (8), 93 (100). Anal. Calcd for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found: C, 74.92; H, 9.66.

*cis*(1′,5′)-(3E)-4-(2′,5′,6′,6′-Tetramethyl-2′-cyclohexen-1′-yl)but-3-en-2-one (cis-α-Irone, 2). A solution of acid 10 (168 mg, 0.81 mmol) in 10 mL of dry ether under N$_2$ was cooled to −55 °C, and methyllithium (1.3 mL of a 1.6 M solution in ether, ca. 2 mmol) was added with vigorous stirring over 1 min. The homogeneous solution was stirred 5 min at −55 °C, warmed up to 0 °C during 20 min, and then refluxed for 90 min. The heterogeneous reaction mixture was cooled and then transferred with a dry syringe to a vigorously stirred solution of 0.1 N HCl (25 mL). [The flask was rinsed with ether (2 × 3 mL) under N$_2$ with a dry syringe.] After 5 min, the mixture was extracted with ether (3 × 100 mL). The combined organic extracts were dried over MgSO$_4$, filtered, and concentrated in vacuo. The residual oil was chromatographed on silica gel (5 g) with pentane/ether (11:1) as eluent. The appropriate fractions were combined and distilled [Kugelrohr, 130 °C (1 mmHg)] to give 148 mg (89%) of (±)-cis-α-irone (2) as a colorless liquid. No other irone isomers could be detected by capillary GC and $^1$H NMR (400 MHz).[13] $^1$H NMR (400 MHz, CDCl$_3$) δ 0.71 (s, 3 H), 0.86 (s, 3 H), 0.87 (d, $J$ = 7 Hz, 3 H), 1.43–1.51 (m, 1 H), 1.53 (m, 3 H), 1.69–1.81 (m, 1 H), 1.90–2.00 (m, 1 H), 2.28 (s, 3 H, CH$_3$CO), 2.55 (br d, $J$ = 11 Hz, 1 H), 5.52 (m, 1 H), 6.12 (d, $J$ = 16 Hz, 1 H), 6.65 (dd, $J$ = 11, 16 Hz, 1 H), MS (70 eV) $m/z$ 206 (6, M$^+$), 191 (2), 136 (41), 121 (100), 109 (10), 93 (73), 91 (17), 77 (14), 43 (39).

## Electronic Structure of 2,4-Methano-2,4-didehydroadamantane: A [3.1.1]Propellane. Photoelectron and Semiempirical Studies

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Since the first syntheses of small propellanes[1] this intriguing class of compounds has been intensively investigated, both experimentally[2–8] and theoretically.[2,3,9,10] Recently, a photoelectron spectroscopic study (PE) of the smallest homologue of the propellane family, [1.1.1]propellane (1), was carried out.[11] The most remarkable feature of its PE spectrum was the appearance of an extremely narrow ionization band corresponding to the highest occupied molecular orbital of 1, indicating that electron ejection from the HOMO leads only to a minute change in the geometry of the molecular frame. Lack of a geometry change accompanying the transition 1 → 1$^+$ might be, as pointed out in ref 11, a consequence of the nonbonding or slightly antibonding character of the HOMO of 1, but it could also be due to the rather tight cage structure of 1, which makes geometry distortions very difficult. The results of recent ab initio[4] and PRDDO[12]

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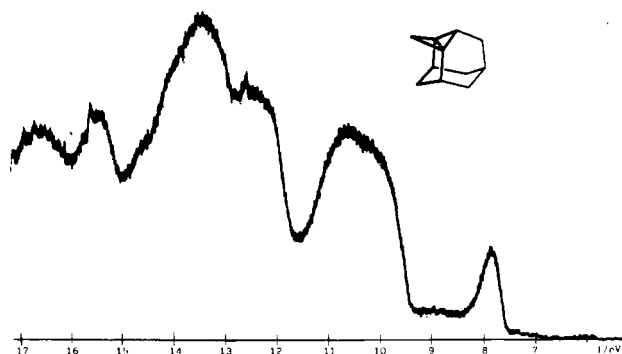(11) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172.

**Figure 1.** He I PE spectrum of [3.1.1]propellane **2**.

**Table I. Vertical Ionization Energies, $I_{vj}$,[a] and Calculated Orbital Energies, $\epsilon_j$, of 2,4-Methano-2,4-didehydroadamantane (2) and 2,4-Methanoadamantane (3)**

| compd | $I_{vj}$, eV | HAM/3[a] | MNDO, $-\epsilon$, eV | orbital |
|---|---|---|---|---|
| **2** | 7.9 | 8.36 | 9.38 | 19a' |
|  |  | 9.96 | 10.91 | 10a'' |
|  |  | 10.26 | 11.00 | 18a' |
|  | 10.0–11.5 | 10.51 | 11.76 | 9a'' |
|  |  | 10.72 | 11.84 | 8a'' |
|  |  | 10.82 | 11.96 | 17a' |
| **3** | 9.3 | 9.86 | 11.00 | 19a' |
|  | 9.7 | 9.81 | 11.04 | 11a'' |
|  | 10.0 | 10.25 | 11.27 | 18a' |
|  | 10.5 | 10.56 | 11.63 | 10a'' |
|  | 10.7 | 11.05 | 12.09 | 9a'' |
|  | 11.0 | 11.10 | 12.15 | 17a' |
|  | 11.3 | 11.50 | 12.40 | 8a'' |
|  | 11.6 | 11.54 | 12.44 | 16a'' |

[a] The HAM/3 results are based on the geometry derived by the MNDO method.[18]

calculations reinforce the conclusion that bridgehead atoms in **1** are indeed "bonded" in the ground state.

Despite a considerable interest in the electronic structure of small propellanes,[2–12] particularly with respect to the nature of the highest occupied MO, PE data are quite scarce.[2,11] In this paper we report the results of a PE spectroscopic investigation of 2,4-methano-2,4-didehydroadamantane[7] (**2**), a prototype [3.1.1]propellane. In
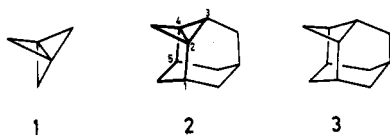


addition, the PE spectrum of its dihydro congener, 2,4-methanoadamantane[7,13] (**3**) will be briefly discussed for comparison. The PE spectrum of **2** is shown in Figure 1, and the relevant PE data are summarized in Table I. To interpret the spectra we compare the first ionization bands with the results of MNDO[14] and HAM/3[15] molecular orbital calculations (viz., Table I) assuming the validity of Koopmans' theorem.[16] Since the geometries of **2** and **3** have not been experimentally determined, we optimized their structural parameters within the MNDO scheme. MNDO was chosen on the basis of its good performance in predicting the structure of the [3.1.1]propellane unit[17]

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**Table II. MNDO-Calculated Orbital Energy Variation for the Highest Occupied Orbitals of 2 upon $C_2$-$C_4$ Stretching**

| | $-\epsilon$, eV | | | |
|---|---|---|---|---|
| $d_{C_2-C_4}$, Å | 19a' | 18a' | 10a'' | 9a'' |
| 0.786[a] | 9.38 | 11.09 | 11.49 | 11.71 |
| 0.85 | 8.89 | 11.00 | 11.09 | 11.82 |
| 0.95 | 8.41 | 10.97 | 11.23 | 11.91 |
| 1.05 | 8.25 | 10.85 | 11.21 | 11.89 |

[a] Optimized geometry.

as evidenced by a comparison with the available X-ray data for an aza[3.1.1]propellane derivative.[6] The structural parameters estimated for the cyclobutane segment of **3** parallel those derived from an electron diffraction experiment on [3.1.1]bicyclohexane.[19]

Perusal of the data presented in Table I shows that both MNDO and HAM/3 reproduce the essential features of the measured PE spectrum of propellane **2**, despite some numerical discrepancies. More specifically, they predict a large separation between the HOMO and the lower occupied orbitals. The spacing of the lower lying orbitals is satisfactorily reproduced as well. Consequently, we assigned the lowest ionization band to the ionization from the molecular orbital (MO) localized in the region between the inverted carbons ($C_2$ and $C_4$). Its rather Gaussian shape with a bandwidth at half height (bwhh) of ca. 0.45 eV, being significantly larger than the bwhh of the first band of **1** (ca. 0.25 eV),[11,20] suggests that the HOMO of **2** has a bonding character. This is in accordance with the chemical behavior[7] of **2** and is supported by the MNDO results (Table II) for the variation of $\epsilon$(HOMO) upon elongation of the distance between inverted carbons. In contrast to propellane **2**, the results of ab initio[10b,d] as well as MNDO[17] calculations for propellane **1** indicate a significant decrease in the energy of the HOMO upon stretching of the interbridgehead distance.

Another point of interest is the pronounced lowering of the first ionization energy of **2** relative to the corresponding entity in **1**. This can be due to an increased $\sigma$ electron pool in **2** caused by its substantially larger $\sigma$ skeleton. Other factors, such as the change in the s character[21] of the HOMO encompassing the inverted carbon atoms and the change in the dihedral angle between cyclopropane rings,[22] may be important too. Ejection of electrons from the lower lying orbitals of **2** give rise to a broad overlapping which prevents accurate correlations between the calculated and experimental ionization energies. The calculations predict five ionization events for the second band. Among these, 10a'' and 8a'' MO's are predicted to be predominantly localized in the [3.1.1]propellane subunit, while 18a', 9a'', and 17a' MO's are found to be more evenly distributed over the entire molecular framework.

The PE data for **3** are of interest in so much as they provide a direct insight into the change of the energies and

(17) For instance, the calculated MNDO distance between the inverted carbon atoms ($C_2$ and $C_4$) in **2** is 1.572 Å,[18] which should be compared with the experimental value of 1.574 Å in the aza [3.1.1]propellane derivative.[6]

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(20) It should be noted, however, that this is still significantly lower than the typical bwhh for PE bands of structurally related saturated hydrocarbons (see: Kimura, K.; Katsumata, S.; Achiba, Y.; Amazaki, T.; Iwata, S. *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Socieities: Tokyo, 1981).

(21) For example, populations of the 2s orbitals of the inverted carbons in the HOMO of **1** and **2** are 0.09 and 0.01,[18] respectively. Since 2s orbitals have lower energies, the HOMO of former molecule should be more stable. This is borne out by the PE spectra.

(22) Gleiter, R. *Topics in Current Chemistry*, Springer-Verlag: Berlin, 1979; Vol. 86, pp 197–285.

composition of the highest occupied orbitals on passing from a [3.1.1]propellane derivative to its dihydro counterpart. The measured PE spectra differ considerably (see Table I). The lowest two, partially resolved, ionization bands of **3** appear at 9.3 and 9.7 eV, respectively, being thus considerably higher than the lowest ionization band of **2**. The compositions of the corresponding MO's, as revealed by the calculated MNDO and HAM/3 wave functions, are quite different. For **2**, as mentioned above, a strong localization of the HOMO between two inverted carbons is observed. In contrast, the two top occupied orbitals of **3** encompass the entire carbon skeleton and get the highest contributions from the carbon atoms forming the cyclobutane unit. Therefore, it is not surprising that the split between the first two bands in **3** roughly corresponds to that found in other alkyl-substituted cyclobutane derivatives.[22] For the third and fourth MO's of **3**, which appear as shoulders to the second and third band respectively, the calculations also predict a high localization at the cyclobutane subunit. In fact, they bear a strong resemblance to the $4a_1$ and $1b_1$ MO of cyclobutane[22,23] (assuming $D_{2h}$ symmetry for the cyclobutane moiety). The higher energy region of the PE spectrum of **3** is characterized by highly overlapping bands starting from ca. 10.3 eV. Their assignment, proposed in Table I, is tentative. More accurate geometries, provided by experiment or advanced ab initio calculations, and additional PE data for structurally related compounds are necessary for a more reliable assignment.

To summarize, the present study indicates that the HOMO of the [3.1.1]propellane **2** has a bonding character. This is evidenced by the Gaussian shape of the first band in the measured PE spectrum and supported by the MNDO calculations of the changes in HOMO energies upon elongation of the distance between inverted carbon atoms. The rather low first ionization energy of **2** is in line with the negligible[21] 2s orbital population at the inverted carbons in the HOMO and the inductive influence of the large $\sigma$ molecular skeleton of adamantane in which [3.1.1]propellane unit is embedded. It appears that the stability of the HOMO in small propellanes may be significantly influenced by the enlargement of the molecular frame, affecting their reactivity in frontier orbital controlled reactions.[24]

## Experimental Section

The [3.1.1]propellane **2** and its dihydro congener **3** were prepared following the procedures described in ref 7. Propellane **2** was trapped into a liquid nitrogen cooled trap and used for the PE measurements immediately after preparation. Prior and during measurements, **2** was kept in this trap at −10 °C in a dry nitrogen atmosphere or in vacuo.

The PE spectra of **2** and **3** were recorded on a Vacuum Generators UV-G 3 instrument using the He I line for excitation. The spectra were recorded at room temperature and were calibrated with xenon.

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## Amide Activation for Cyclopropane Ortho Lithiation

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We recently found that the well-known[1] activation by amides for ortho lithiation of aromatics and other unsaturated systems could be extended to the "saturated" cubane system.[2] As cubane (31% s) and cyclopropane (33% s) have similar C–H bonding parameters,[3] we looked to see whether the chemistry we were developing for cubanes also applied to cyclopropanes.[4] Our preliminary results, detailed here, are encouraging.

Reaction of 1-methyl-1-(*N,N*-diisopropylcarbamoyl)-cyclopropane (**1**)[5] with 8 equiv of lithium tetramethylpiperidide (LiTMP) in THF at 0 °C gives partial conversion to the ortho-lithiated derivative **2**. On quenching with $CH_3OD$, the starting material is substantially recovered with approximately 60% monodeuterium incorporation as determined by mass spectral analysis (CI, isobutane[6]). NMR analysis places the deuterium atom on the cyclopropane ring, necessarily $\beta$ to the amide group. It is predominately, perhaps exclusively, cis to the amide.

Following the lead provided by our cubane work, we treated compound **1** with excess LiTMP/$HgCl_2$. Complete conversion to the organomercury occurs quickly via transmetalation of the intermediate ortho-lithiated compound **2**. The equilibrium lies well to the right. The organomercury **3** (X = Cl) can be isolated easily as its chloride.

Reaction of **3** with iodine in $CHCl_3$ gives the *cis*-iodoamide **4**, pure and crystalline, in 81% yield. The cis geometry was inferred (albeit arguably) from NOE experiments[7] and then confirmed definitively by single-crystal X-ray analysis. Interestingly, and unexpectedly,[8] iodination of **3** in pyridine gives both cis and trans iodoamides, favoring **4** by 2:1, each configurationally stable in the reaction medium.

"Reverse transmetalation", as defined elsewhere,[2b] occurs cleanly on treatment of **3** with $CH_3Li$. This makes available stoichiometrically the organolithium **2**, free of interfering reagents.[9] The transmetalation equilibrium

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(3) Cf.: Luh, T.-Y.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 3712.

(4) It is very difficult to lithiate cyclopropanes by reaction with alkyllithiums. Certain examples of remote activation are known; cf. Section 2.2.2 in ref 1c.

(5) Prepared in standard fashion via the acid chloride ($SOCl_2$) from the commercially available acid (Aldrich): **1**, mp 57–58 °C, from hexane.

(6) Chemical ionization was used for under electron impact conditions self-CI of *N,N*-diisopropylamides is a complication to quantitative MS analysis.

(7) These experiments were done in collaboration with Dr. J. S. Witzeman.

(8) Jensen, F. R.; Rickborn, B. *Electrophilic Substitution of Organomercurials*; McGraw-Hill: New York, 1968; p 86 ff.

(9) The organic byproduct is $(CH_3)_2Hg$, which is toxic and volatile. Due caution is called for. We used reaction with iodine at the end of our reaction sequences to obviate the problem. Butyllithium used instead of $CH_3Li$ in the reverse transmetalation gives the less hazardous dibutylmercury.