

such a deformation of $k = 483 \text{ N m}^{-1}$ for **1** and $K = 640 \text{ N m}^{-1}$ for **1**⁺. This result contradicts what is observed (and by far!) if one assumes that only totally symmetric vibrational modes are stimulated by electron ejection from $3a_1'$. One, as yet unexplored, explanation for the observed, close spacing of the vibrational fine structure of band 1 could be looked for in the vibronic mixing of the $^2A_1'$ ground state of **1**⁺ with the first excited $^2E''$ state, which are only $\sim 1.0 \text{ eV}$ apart (adiabatically).

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Registry No. 1, 35634-10-7.

Rotational Spectra and Structures of Small Clusters: Ar₃-HF and Ar₃-DF

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Previous studies of microwave rotational spectra for van der Waals and hydrogen bonded complexes have been limited to binary species like Ar-HF^{1,2} and (HF)₂.³⁻⁵ Herein we demonstrate the feasibility of extending such studies to small molecular clusters. In particular, we report the characterization of Ar₃-HF and Ar₃-DF, in which the H/DF lies along the threefold (*c*) axis of the Ar₃ group, with the H/D end closest to Ar₃. The symmetric top transitions observed for $J = 1 \rightarrow 2$ through $J = 6 \rightarrow 7$ are fitted by rotational constants B_0 , D_J , and D_{JK} of 1188.212 MHz, 6.85 kHz, and -5.76 kHz for Ar₃-HF and of 1180.379 MHz, 6.57 kHz, and -5.15 kHz for Ar₃-DF. The composition of the clusters is established by hyperfine structure of the transitions, by the absence of *K* states other than 0, ± 3 , and ± 6 , and by the values found for B_0 .

The spectra were observed with the Flygare Mark II spectrometer.⁶ It combines the principles of pulsed Fourier transform spectroscopy, a Fabry-Perot cavity, and synchronization of the microwave pulse with a pulsed beam of a gas mixture from a supersonic nozzle which cools the gas mixture and helps generate the molecular complexes.⁷ Detection of the cluster was made possible by modifications in the spectrometer which increased S/N about 10-fold by better utilization of its inherent sensitivity.⁸ The main improvements were the use of several microwave pulses after each gas pulse, a 10-fold increase in the repetition rate of the gas pulse, and mounting the gas nozzle to enable ready adjustment of its distance from the axis of the Fabry-Perot mirrors. Also, a microwave coupling system was developed to extend the cavity's operating range to C band (4-8 GHz).⁸

Argon was used as the carrier gas with 0.5-1.0% of HF and/or DF added. At the nozzle the gas mixture was at ambient temperature and 1 atm. The nozzle diameter was 0.94 mm. Under these conditions Ar-HF and (HF)₂ are readily observed,¹⁻⁴ and small clusters of Ar_{*n*}^{9,10} and (HF)_{*n*}³ are generated at concentrations

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Table I. Observed and Calculated Frequencies of the Rotational Transitions for Ar₃-HF^a

<i>J, K</i> → <i>J', K'</i>	obsd, MHz	calcd, MHz	difference, kHz
1,0 → 2,0	4752.628	4752.630	-2
2,0 → 3,0	7128.533	7128.535	-2
3,0 → 4,0	9503.944	9503.946	-2
3,±3 → 4,±3	4.37 ^b	4.362	
4,0 → 5,0	11878.699	11878.700	-1
4,±3 → 5,±3	9.21 ^b	9.219	
5,0 → 6,0	14252.636	14252.632	4
5,±3 → 6,±3	3.257	3.254	3
6,0 → 7,0	16625.579	16625.578	1
6,±3 → 7,±3	6.300	6.303	-3
6,±6 → 7,±6	8.479	8.479	0

^a Transition frequencies for states with $K \neq 0$ are emphasized by omitting the first 3 or 4 digits, which are the same as for the transition just above. ^b Approximate center of partially resolved hyperfine structure; not used in determination of rotational constants.

Table II. Observed and Calculated Frequencies of the Hyperfine Components in the $K = 0, J = 1 \rightarrow 2$ Transitions

components		obsd, MHz	calcd, MHz	difference, kHz
<i>J, F₁, F</i>	→ <i>J', F'₁, F'</i>			
Transition at 4752.628 MHz for HF Species				
1, ³ / ₂ , 2	2, ³ / ₂ , 2	2.597	2.597	0
1, ¹ / ₂ , 0	2, ³ / ₂ , 1	2.603	2.602	1
1, ¹ / ₂ , 1	2, ³ / ₂ , 2	2.628	2.628	0
1, ³ / ₂ , 1	2, ⁵ / ₂ , 2		2.628	0
1, ³ / ₂ , 2	2, ³ / ₂ , 3		2.630	-2
1, ¹ / ₂ , 1	2, ³ / ₂ , 1	2.679	2.678	1
Transition at 4721.304 MHz for DF Species				
1, 1, ³ / ₂	2, 1, ³ / ₂	1.215 ^a	1.216	-1
1, 1, ¹ / ₂	2, 2, ³ / ₂	1.300	1.298	2
1, 2, ³ / ₂	2, 3, ⁵ / ₂		1.299	1
1, 2, ³ / ₂	2, 3, ⁷ / ₂		1.301	-1
1, 1, ³ / ₂	2, 2, ⁵ / ₂	1.307	1.306	1
1, 0, ¹ / ₂	2, 1, ³ / ₂	1.341	1.343	-2

^a The first 3 digits are omitted.

decreasing with *n*. Also, mixed species Ar_{*n*}-(HF)_{*m*} are formed, with Ar-(HF)₂ and Ar₂-HF expected to predominate.¹⁰ Indeed, we have observed a large number of transitions attributed tentatively to Ar₂-HF (T shaped), Ar-(HF)₂, and a noncyclic (HF)₃. The most fully characterized species, however, is a symmetric top, which has the more readily identifiable transitions listed in Table I for HF. They were fitted by the usual Hamiltonian including centrifugal distortion.¹¹ An equivalent set of transitions was observed at somewhat lower frequencies with DF.

Although the $J = 0 \rightarrow 1$ transitions are below the present frequency range, the weaker, less extensive hyperfine structure was observed for the $K = 0, J = 1 \rightarrow 2$ transitions² (Table II). It establishes the presence of an H/DF molecule at the figure axis of the symmetric top, without perturbations from other $I \neq 0$ nuclei. The hyperfine structure was fitted as done earlier² for the Ar-HF and Ar-DF dimers. The adjustable parameters are the line center and the "average" torsional angle α between the H/DF axis and the *c*-inertial axis, which reduces the hyperfine interactions by the factor $(3 \cos^2 \alpha - 1)/2$. The values found for α in the HF and DF species are 41.0 (2)° and 35.6 (4)°, compared with 41.1° and 32.7° reported for the dimers.² The similarity indicates the equilibrium configuration has the H/DF axis along the *c* axis.

Transitions were observed for only two nonzero *K* states, assigned in Table I as $K = \pm 3$ and ± 6 .¹² An alternate assignment is as $K = \pm 1$ and ± 2 , with the higher states too weak for detection. This is precluded, however, by the observed partially resolved lines listed as $K = \pm 3$ for $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$. They extend over ~ 50 and 20 kHz , respectively, in accord with calculations

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for $K = \pm 3$, while much narrower widths (≤ 5 kHz) are predicted for $K = \pm 1$. For K states other than 0, ± 3 , and ± 6 to be forbidden, the symmetric top must have a 3-fold axis associated with three zero-spin nuclei.¹¹ These criteria are met by the molecular cluster $^{40}\text{Ar}_3\text{-H/DF}$, which is an oblate symmetric top.

Confirmation of this composition is provided by analysis of B_0 . Neglecting any tilt of the Ar_3 plane and vibrations other than torsional oscillations of the H/DF, we have¹³

$$I_{bb}(\text{cluster}) = (1/2)(1 + \cos^2\alpha)I_{bb}(\text{H/DF}) + I_{bb}(\text{Ar}_3) + \mu_c R^2 \quad (1)$$

where R is the distance between the H/DF and Ar_3 centers of mass (c.m.) and $I_{bb}(\text{Ar}_3)$ is a function of r , the Ar-Ar distance. For argon dimer, a B_0 of 0.05778 cm^{-1} has been determined from a high-resolution Raman study.¹⁴ It gives an r_0 of 3.821 \AA , which in eq 1 leads to values of 2.785 and 2.479 \AA for R in $\text{Ar}_3\text{-HF}$ and -DF . The smaller R for the DF species show that the H/D end is pointed at the Ar_3 . The corresponding H/DF c.m. to Ar distances of 3.553 and 3.525 \AA are comparable with the 3.510 and 3.461 \AA found in Ar-H/DF .² Also, the H/DF c.m. to Ar line is 38.5° from the c axis. A full account will be presented later, including the results of a search for the isotopic species $^{36}\text{Ar}^{40}\text{Ar}_2\text{-H/DF}$ to determine accurate bond distances.

Registry No. Ar, 7440-37-1; HF, 7664-39-3; DF, 14333-26-7.

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Synthesis, Trapping, and Spectral Characterization of 1H-Cyclopropa[1]phenanthrene¹

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The cycloproparenes **1**,³ **2**,⁴ and **3**,⁵ and their derivatives are surprisingly stable, readily available materials.⁶ By comparison cyclopropa[*a*]naphthalene (**4**) explodes upon melting^{7a} and its 1,1-difluoro derivative^{7b} is stable in solution only at temperatures below -30°C . This decrease in stability perhaps reflects the formally enhanced olefinic character of the bridge bond. 1H-Cyclopropa[1]phenanthrene (**5**), the most important unknown structural variant within this family, should exemplify further this

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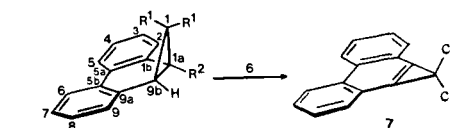
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Scheme I

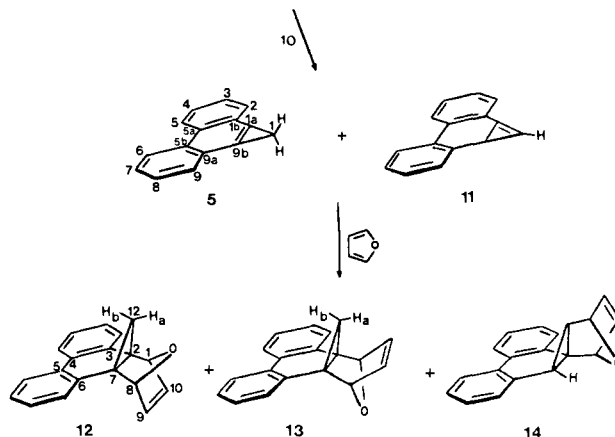


6 $R^1 = \text{Cl}$; $R^2 = \text{Se(O)Ph}$

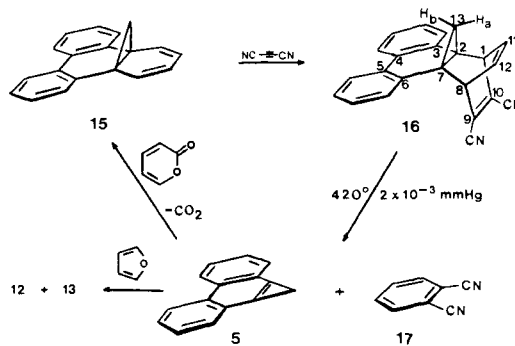
8 $R^1 = \text{H}$; $R^2 = \text{SeMe}$

9 $R^1 = \text{H}$; $R^2 = \text{SeMe}_2 \text{BF}_4^-$

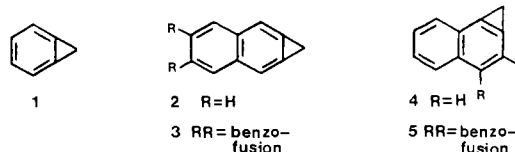
10 $R^1 = \text{H}$; $R^2 = \text{Se}^+ \text{MeCH}_2^-$



Scheme II



phenomenon. We now report syntheses of **5** and show it to be an unusually reactive molecule stable only at low temperatures.



Recent results have shown⁸ that *syn*-selenoxide elimination from **6** (Scheme I) occurs to give products derived from **7**. However, **7** could be neither isolated nor trapped because of facile cleavage of the three-membered ring. Despite its limitations, the study⁸ has provided the first definitive evidence for the existence of the 1H-cyclopropa[1]phenanthrene ring system and implies that an elimination across the 1a,9b-positions of an appropriate 1a,9b-dihydro derivative is the method of choice^{6,8,9} for the synthesis of **5**.

With this in view, selenide **8**^{10,11} has been transformed into the selenonium salt **9** which eliminates dimethyl selenide upon

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(10) Compound **8** is available from 9-bromophenanthrene in five steps: Dent, B. R.; Halton, B., manuscript in preparation.

(11) All new compounds reported provided satisfactory analytical and spectral data.