TABLE I

Molecule	R, Å.	Ionicity, %	Energy of formation from elements, kcal./mole $G(g) + n/2A_2(g) \rightarrow GA_n(g)$	Dissociation energy per bond, kcal./mole $1/nGA_n(g) \rightarrow 1/nG(g) + A(g)$
XeF_4	1.92	58	−123.1	49.6
KrF_4	1.72	49	− 23.5	24.4
	1.72	55	− 53.0[a]	31.7[a]
	1.78	47	− 0.5	18.8
	1.78	52	− 25.8[a]	25.1[a]
ArF_4	1.60	53	30.7	11.0
	1.64	51	53.7	5.3
NeF_4	1.40	33	507.1	−108.1
$XeCl_4$	2.30	45	50.9	15.8
	2.34	44	61.1	13.3
$KrCl_4$	2.11	37	137.4	− 5.8
	2.11	40	132.3[a]	− 4.6[a]
XeF_2	1.98	63	− 11.1	24.2
KrF_2	1.72	63	5.3	16.1
$XeCl_2$	2.30	54	42.9	7.1

[a] Calculated using an extrapolated value of 52.5 e.v. for the fourth ionization potential of Kr.

available to permit calculations for halides of this element. However, the trends in Table I make it fairly certain that if the data were available, calculation would predict RnF_4 and RnF_2, and perhaps $RnCl_4$ as well.

Another interesting feature is the sharp break in the sequence of predicted energies between the halides of argon and neon. While the decrease in calculated bond energy of the fluorides is slow enough from xenon to argon so that ArF_4 is still a possibility, the sudden drop between argon and neon virtually guarantees that neon halides cannot exist.

The present results indicate that the inert gas halides fit naturally into the sequence of halides of the nonmetallic elements in their higher valence states, and that no special bonding assumptions are needed.

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THE BONDING IN THE INERT GAS-HALOGEN COMPOUNDS—THE LIKELY EXISTENCE OF HELIUM DIFLUORIDE

Sir:

In 1951, Pimentel discussed the bonding in trihalide ions in terms of a simple molecular orbital description.[1] In this widely ignored paper, the applicability of the bonding scheme to other molecular species was recognized and, in fact, the existence of inert gas–halogen compounds was predicted. "*It is to be expected that a rare gas could form complexes with halogens.*"[1] At about the same time, Hach and Rundle[2] discussed bonding of trihalides in similar terms, though without any reference to possible inert gas compounds.

Since then there has appeared significant support for this molecular orbital description of the trihalides through electric quadrupole resonance studies[3,4] and infrared studies.[5] The quadrupole coupling constants in both ICl_2^- and ICl_4^- confirm the proposal that d orbitals do not contribute significantly to the bonding.

The recent preparation of inert gas compounds has naturally stimulated much interest in their bonding.[6–9] Among these discussions, there has appeared a revival of the molecular orbital description proposed by Pimentel[8,9] and, we feel, the model provides a simple and sufficient basis for explaining the existence of such compounds as XeF_2. The ease of extension of the scheme to such compounds as ICl_4^- and XeF_4 has been amply pointed out by others[4,5,8,9] and need not be reproduced here.

There is, however, one other aspect of the molecular orbital description offered by Pimentel[1] that deserves consideration. The essential similarity of the molecular orbital descriptions of HF_2^- and I_3^- was noted[1] and remarked upon again by Pimentel and McClellan.[10] Experimental support for this connection has also appeared[11] and we are encouraged to explore its implications in reference to inert gas chemistry. In particular, *the compound HeF_2 can be expected to be stable.*

The molecular orbital description of HF_2^-, based upon the halogen axial 2p orbitals and the hydrogen 1s orbital,[1] need not be repeated here and its applicability to the isoelectronic molecule HeF_2 is obvious. We can, however, make some comparisons between HF_2^- and HeF_2 that may aid in searching for this interesting molecule. A rough estimate of the infrared spectrum of HeF_2 can be based upon that of HF_2^-. The vibrational frequencies and a set of force constants for HF_2^- are shown in Table I.[12] These force constants transferred to HeF_2 lead to the predicted frequencies shown in the second row of Table I. We feel, however, that the spectrum of XeF_2 is relevant here. Smith has concluded[13] that the ratio f_{rr}/f_r is much smaller for XeF_2 than for the trihalide ions. We do not share his view that this difference vitiates the molecular orbital bonding description, for a reasonable rationale can be formulated to explain it. The molecules XeF_2 and ICl_2^-, though isoelectronic (in bonding electrons), involve quite different formal charge distributions. The proposed molecular orbitals tend to place somewhat less than one electron charge on the central atom and somewhat more than 1½ electron charges on the terminal atoms. In the case of ICl_2^-, the formal charge implication is that the excess charge of the ion is distributed on the chlorine atoms and the iodine atom has a charge near zero. The case of XeF_2 contrasts since the central atom must have a significant positive formal charge to balance the negative charge placed on the terminal atoms. This difference can be expected to tend to strengthen the bond somewhat because of the electrostatic attractions, raising f_r.[14] At the same time, the

TABLE I

THE VIBRATIONAL POTENTIAL FUNCTION AND FREQUENCIES OF HF_2^- (EXPERIMENT) AND HeF_2 (PREDICTED)

	Frequency, cm.$^{-1}$ ν_1 (Raman active)	ν_2 (Infrared active)	ν_3 (Infrared active)	Bond length, Å	Force constant[a] f_r	f_{rr}	f_α
HF_2^-	600	1230	1425	1.13	2.31	1.72	0.28
HeF_2	600	640	743	1.13	2.31	1.72	.28
HeF_2	585	673	1600	1.08	3.47	0.35	.28

[a] f_r = bond stretching force constant (in millidynes/Ångstrom); f_{rr} = bond stretching interaction force constant (in millidynes/Ångstrom); f_α = angle bending force constant (in millidyne-Ångstrom/radian).

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(1) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(2) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).

(3) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

(4) R. S. Yamasaki and C. D. Cornwell, *ibid.*, **30**, 1265 (1959).

(5) W. B. Person, G. R. Anderson and J. D. Fordemwalt, *ibid.*, **35**, 908 (1961).

(6) L. C. Allen, *Science*, **138**, 892 (1962).

(7) L. C. Allen and W. deW. Horrocks, Jr., *J. Am. Chem. Soc.*, **84**, 4344 (1962).

(8) K. S. Pitzer, *Science*, **139**, 414 (1963).

(9) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., 1960, p. 343.

(11) W. B. Person, R. E. Humphrey and A. I. Popov, *J. Am. Chem. Soc.*, **82**, 29 (1960).

(12) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 781 (1954).

(13) D. F. Smith, *ibid.*, **38**, 270 (1963).

interaction force constant should be reduced, because an asymmetric displacement is no longer energetically favored over a symmetric displacement. In the symmetric mode, the terminal atom repulsions that tend to raise the energy are counteracted by the central atom positive charge.

In view of these considerations, we feel that a more educated guess of the force constants for HeF_2 is possible. In the last row of Table I, we propose a more likely potential function (and an appropriately shortened bond length) together with the implied frequencies.

Though the two sets of predicted frequencies are discordant, they show that the infrared absorptions should fall in a readily accessible region. A search for this species, HeF_2, is in progress here.

(14) A prototype effect is noted in the successively shorter bond lengths of ClO_2^- (1.64 Å.), ClO_3^- (1.57 Å.) and ClO_4^- (1.50 Å.), which also can be associated with the accumulating formal charge on the central atom.

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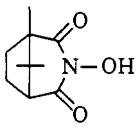
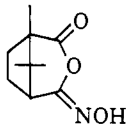
AN UNUSUAL NEF REACTION. THE REARRANGEMENT OF 3-NITROCAMPHOR

Sir:

We wish to report the rearrangement of 3-nitrocamphor to N-hydroxycamphorimide (I) by acid catalysis. The reaction illustrates a variation of the direct Nef reaction[1] by acid catalyzed hydrolysis. The product of the isomerization was formulated as an oximino compound (II) by Lowry,[2] who rejected the alternative structure. Synthesis of the N-hydroxyimide establishes I as the structure for the product of the rearrangement.

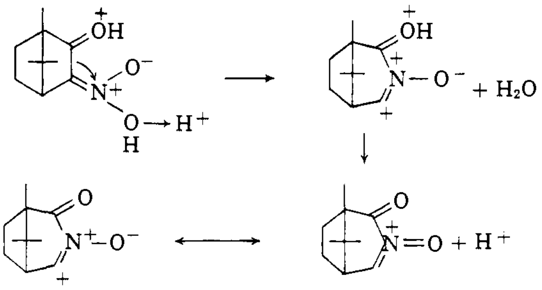

I


II

Camphoric anhydride was treated with N-benzyloxyamine according to the method of Ames and Grey[3] to form N-benzylcamphorimide (III), m.p. 80–81°; $[\alpha]^{23}D$ +19.2° ($CHCl_3$). (*Anal.* Calcd. for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found C, 70.99; H, 7.38; N, 4.97.) Hydrogenolysis of III gave the N-hydroxyimide (I) in 51% yield, m.p. 229–230°, $[\alpha]^{23}D$ +7.29° (*Anal.* Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.60; H, 7.65; N, 7.20). Absorption in the infrared spectrum characteristic of the N-hydroxyimide group[3] occurred at 3.0, 5.74, and 5.95 μ.

The rearrangement of 3-nitrocamphor with concentrated hydrochloric acid gave N-hydroxycamphorimide in 94% yield, m.p. 229–230°; $[\alpha]^{23}D$ +7.46° ($CHCl_3$). (*Anal.* Found: C, 60.76; H, 7.58; N, 7.18.) The infrared spectra of the N-hydroxyimides formed by rearrangement and by synthesis were identical.

The unusual course of the Nef reaction, in contrast to the normal Nef reaction, must be effected by protonation of the carbonyl group in 3-nitrocamphor to facilitate the cleavage of the C–C bond and the migration of the carbonyl carbon atom with the electrons to form the C–N bond which occurs concertedly with the acid catalyzed dehydration of the nitronic acid. Loss of a proton forms the carbonyl group. Protonation and hydration of the resulting intermediate would lead to I with the development of a carbonyl group by elimination of the catalyst. The rearrangement involves a 1,2-shift with ring expansion.



The rearrangement of 3-nitrocamphor with sodium hydroxide and benzoyl chloride forms the benzoate of I in a yield of 46%, m.p. 136–137°; $[\alpha]^{23}D$ +9.73° ($CHCl_3$). (*Anal.* Calcd. for $C_{17}H_{19}NO_4$: C, 67.75; H, 6.35; N, 4.65. Found: C, 67.76; H, 6.20; N, 4.76.) The benzoyl derivative of N-hydroxycamphorimide was prepared in the usual way, m.p. 136–137°; $[\alpha]^{23}D$ +9.76° (*Anal.* Found: C, 68.01; H, 6.65; N, 4.93.) The infrared spectra of the benzoyl derivatives were identical. Similar rearrangements of α-nitro ketones have not been reported. The product of the rearrangement was previously formulated as a derivative of II.

Treatment of 3-nitrocamphor with acetic anhydride forms N-acetoxycamphorimide in 45% yield, m.p. 116–117°; $[\alpha]^{24}D$ +6.43° ($CHCl_3$) (*Anal.* Calcd. for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.22; H, 7.22; N, 5.82.) The acetate was prepared from I, m.p. 116–117°, $[\alpha]^{24}D$ +6.69°. (*Anal.* Found: C, 60.53; H, 7.01; N, 6.07.) The infrared spectra were identical.

Further work is in progress on the rearrangements of α-nitro ketones.

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(1) H. Feuer and A. T. Nielsen, *J. Am. Chem. Soc.*, **84**, 688 (1962).

(2) T. M. Lowry, *J. Chem. Soc.*, 986 (1898).

(3) D. E. Ames and T. F. Grey, *ibid.*, 631 (1955).

PRIMARY PHOTOPRODUCT OF 2,6-DIMETHYL-4-AMINOPYRIMIDINE

Sir:

During the course of a systematic study of the photochemical (2537 Å.) behavior of a number of 4-aminopyrimidines,[1] one of these, 2,6-dimethyl-4-aminopyrimidine (I), was found to give rise in slightly alkaline medium (0.02 *M* phosphate buffer, pH 8–9) to a single primary photoproduct (II) which, because of its low solubility, crystallized spontaneously during irradiation. The importance of identifying II stems in part from the fact that the photochemical reaction involved appears to be typical of those undergone by other 4-aminopyrimidines[1]; it also bears some resemblance to the reactions exhibited by the 5-substituted cytosine residues found in the DNA of the T-even bacteriophages.[1,2]

Large scale preparation of II was achieved in better than 50% yield by irradiation of I in specially constructed preparative equipment elsewhere described.[3] Its molecular weight and elementary composition were similar to those for I, suggesting an intramolecular rearrangement. In the ultraviolet the long wave

(1) K. L. Wierzchowski and D. Shugar, 4th Intern. Cong. Photobiol., Copenhagen, 1960 (in "Progress in Photobiology," Elsevier, Amsterdam, 1961, pp. 606–608).

(2) K. L. Wierzchowski and D. Shugar, *Acta Biochim. Polon.*, **7**, 63 (1960).

(3) D. Shugar, in "The Nucleic Acids" (E. Chargaff and J. N. Davidson, ed.), Vol. III, Chapt. 30, Academic Press, Inc., New York, N. Y., 1960.