The Structures of and Bonding in Some A_2X_4 Molecules

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Abstract: Semiempirical SCF and extended Hückel LCAO–MO calculations have been performed on the nominally single-bonded A_2X_4 molecules B_2F_4, B_2Cl_4, N_2H_4, N_2F_4, P_2H_4, and P_2F_4. The major emphasis is placed on attempting to understand the observed conformations and conformational changes in these molecules. For the diboron tetrahalides the total (SCF) molecular energy of the planar (D_{2h}) rotamer is lower than that of the staggered (D_{2d}) rotamer for a given B–B bond distance. For N_2H_4, N_2F_4, P_2H_4, and P_2F_4 total energy and overlap population considerations suggest the order of conformational stability *gauche* > *cis* > *trans*. When applicable or available the agreement between calculated and observed dipole moments, ionization potentials, and nuclear spin coupling constants is also considered.

There has been a considerable interest in the nature of the bonding in A_2X_4 molecules. The molecule N_2O_4 has attracted the most theoretical interest on account of the unusually long nitrogen–nitrogen bond distance in its stable, planar conformation.[1] In the present work, however, we are concerned with A_2X_4 molecules which do not involve any formal double bonds, specifically B_2F_4, B_2Cl_4, N_2H_4, N_2F_4, P_2H_4, and P_2F_4. Hydrazine is, in fact, the first molecule of this type to have been treated theoretically.[2] More recently this molecule has been the subject of *ab initio* LCAO–MO–SCF calculations.[3] Previous studies of the other A_2X_4 molecules comprise a qualitative discussion of the electronic distributions in N_2F_4[4] and B_2F_4[5] in terms of bond order and electroenagtivity considerations, a VESCF treatment[6] of N_2F_4, B_2F_4, and B_2Cl_4, and extended Hückel calculations on B_2F_4[7] and B_2Cl_4.[7,8] However, the two extended Hückel studies appear to reach opposite conclusions regarding the more stable isomer of B_2Cl_4.

Our principal interest in the single-bonded A_2X_4 molecules is equilibrium structure prediction based upon the following criteria: (a) total molecular energy; (b) best agreement with available dipole moment data; and (c) best agreement with nuclear spin coupling constant data. We are also interested in the nature of the bonding in these molecules; special interest is focused on the reasons for the calculated order of conformational stability *gauche* > *cis* > *trans* in the hydrazine-like molecules.

Method of Calculation

The following three approaches were employed.

(i) Semiempirical SCF Calculations Including Overlap (SCF–IO Method). The details of this method, its attendant approximations, and empirical parameterization have been the subject of a previous publication.[9] The method includes all valence electrons which are considered to occupy Slater orbitals, and molecular orbitals are constructed from the atomic orbitals in the usual LCAO fashion.

$$\psi_j = \sum_i^n C_{ij}\phi_i \qquad (1)$$

Use of the variation principle leads to the so-called Roothaan equations[10]

$$\sum_j (F_{ij} - S_{ij}e_u)C_{ju} = 0 \qquad i = 1, 2, 3, \ldots, n \qquad (2)$$

F_{ij}, the elements of the Hartree–Fock Hamiltonian matrix, are specified by

$$F_{ij} = H_{ij} + \sum_k \sum_l P_{kl}[(ij,kl) - \tfrac{1}{2}(ik,jl)] \qquad (3)$$

where P_{kl} is the charge density–bond order matrix and (ij,kl) and (ik,jl) represent the multicenter Coulomb and exchange integrals, respectively. The general form of H_{ij}, the core interaction matrix, is

$$H_{ij} = \int \phi_i\left[-\tfrac{1}{2}\nabla^2 - \sum_A V_A(r)\right]\phi_j\, d\tau \qquad (4)$$

Integration of eq 4 with i equal to j yields

$$H_{ii} = \left(\phi_i^A \middle| -\tfrac{1}{2}\nabla^2 - \frac{Z_A}{r_{1A}} \middle| \phi_i^A\right) - \sum_{B \neq A}\left(\phi_i^A \middle| \frac{Z_B}{r_{1B}} \middle| \phi_i^A\right) \qquad (5)$$

i.e.

$$H_{ii} = U_i^A - \sum_{A \neq B} V_{AB}$$

The core-electron integrals, U_i^A, were taken from Klopman's analysis of spectroscopic data,[11] and the remaining

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Table I. Structural Data on A_2X_4 Molecules

Molecule	Method	Results	Ref
B_2F_4	X-ray	Planar (D_{2h})	*a*
	Electron diffraction	Staggered (D_{2d}) or free rotation	*b*
	Ir + Raman	Staggered or free rotation	*c*
B_2Cl_4	X-ray	Planar (D_{2h})	*d*
	Electron diffraction	Staggered (D_{2d})	*e*
	Ir + Raman	Staggered (D_{2d})	*f*
N_2H_4	X-ray	Probably eclipsed (C_{2v})	*g*
	Neutron diffraction	Probably eclipsed (C_{2v})	*h*
	Microwave	*gauche* (C_2)	*i*
	Electron diffraction	*gauche* (C_2)	*j*
	Ir + Raman	*gauche* (C_2)	*k*
N_2F_4	Microwave	*gauche* (C_2)	*l*
	Electron diffraction	*gauche* (C_2)	*m*
	Ir + Raman	*trans* + *gauche* equilibrium	*n*
	Nmr	*gauche* + *trans*	*o*
P_2H_4	Ir + Raman	Probably *gauche*	*p*
	Nmr	Assumed rapid rotation with effective C_{2v} symmetry	*q*
P_2F_4	Ir + Raman	Probably *trans*	*r*
	Nmr	Assumed *trans*	*s*

[a] Reference 21. [b] Reference 22b. [c] Reference 23c,d. [d] Reference 21. [e] Reference 22a. [f] Reference 23a,b. [g] Reference 25. [h] Reference 26. [i] Reference 28. [j] Reference 27a,b. [k] Reference 29. [l] Reference 36. [m] Reference 40. [n] Reference 38. [o] Reference 39. [p] References 43 and 44. [q] Reference 46. [r] Reference 45. [s] Reference 47.

terms (nuclear attraction integrals) were approximated by the method of Baird, Dewar, and Klopman.[12] In our method the most satisfactory expression for the off-diagonal elements of the core interaction matrix, H_{ij}, was found to be

$$H_{ij}^{AB} = \tfrac{1}{2}\beta_{AB}S_{ij}\left[(U_i^{A} + U_j^{B}) - \left(\sum_{C\neq A} V_{AC} + \sum_{C\neq B} V_{BC}\right)\right] \qquad (6)$$

The physical interpretation of eq 6 is that it is the energy of an electron in the overlap region between two atomic orbitals ϕ_i and ϕ_j on cores A and B, respectively, and as such is proportional to the overlap integral (S_{ij}) between these orbitals, the mean of the core-electron integrals U_i^A and U_j^B, and the mean of the nuclear attraction terms V_{AC} and V_{BC}. β_{AB} is a parameter which depends only upon the nature of cores A and B and is given by the expression

$$\beta_{AB} = \tfrac{1}{2}(\beta_A^0 + \beta_B^0) \qquad (7)$$

The evaluation of these parameters was discussed previously.[9] The following values were employed: H, 1.15; B, 1.111; N, 1.15; F, 1.06; P, 1.115; and Cl, 1.06.

Output of the program (coded in FORTRAN IV and ASCENT 2.0) includes eigenvectors, eigenvalues, the total molecular and electronic energies, and a Mulliken overlap population analysis.[13] In the present treatment we employ the overlap population between atoms A and B, P_{AB} (denoted by TOP in the tables), and between orbitals i and j, P_{ij} (OP), given respectively by

$$P_{AB} = 2\sum_{u}^{occ}\sum_{i}^{A}\sum_{j}^{B} N_uC_{iu}C_{ju}S_{ij} \qquad (8)$$

$$P_{ij} = 2\sum_{u}^{occ} N_uC_{iu}C_{ju}S_{ij} \qquad (9)$$

where N_u is the orbital occupation number of the uth molecular orbital.

The evaluation of ionization potentials, total energies, dipole moments, and nuclear spin coupling constant was discussed in detail earlier.[9] The heats of formation, ΔH_f, were calculated by subtracting the sum of the isolated atom-core energies from the total molecular energies. The energy of the valence electrons in the configuration $(s)^{ns}$ $(p)^{np}$ is given by[14]

$$E(A) = nsU_s^{A} + npU_p^{A} + \tfrac{1}{2}\gamma_{AA}(ns + np)(ns + np - 1) \qquad (10)$$

where γ_{AA} is the one-center Coulomb integral discussed previously.[9]

(ii) Semiempirical SCF Calculations with Complete Neglect of Differential Overlap (SCF-CNDO/2 Method). These calculations were performed using a program written in our laboratories by two of the authors (W. D. W. and M. C. D.) and M. W. Taylor. The program is based on the approximate LCAO-SCF method of Pople and Segal[15] in which differential overlap is neglected. For the second-row elements the bonding parameter values (β^0) and atomic matrix element data have been published by Santry and Segal.[16]

Extended Hückel Calculations (EHT Method). One-electron eigenvectors and eigenvalues were computed using the program developed by Hoffmann.[17] Valence-state ionization potentials[18] are used for the diagonal elements of the H matrix, and the off-diagonal elements

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Table II. Summary of the SCF–IO Results for B_2F_4

Property	Planar[a]	Staggered[b]	Planar[d]	Staggered[c]	Exptl
IP, eV	11.03	11.19	11.04	11.21	...
Total molecular energy, eV	−2058.38	−2057.87	−2057.10	−2056.69	*e*
ΔH_f, kcal/mole	−901.75	−890.12	−872.42	− 863.08	−696.4[f]
Barrier, kcal/mole	11.63[g]		9.34[g]		...
	Orbital Overlap Population (OP)[h]				
$B(p_z)$–$B(p_z)$	0.1460	0.0762	0.1186	0.0617	
$B(p_y)$–$B(p_y)$	0.0351	0.0762	0.0285	0.0617	
$B(p_z)$–$F(p_z)$	0.1598	0.1722	0.1642	0.1743	
	Total Overlap Population (TOP)[i]				
B–B	1.1094	1.0809	1.0470	1.0234	
B–F	0.6868	0.6877	0.6942	0.6950	

[a] The structural information was taken from ref 20. B–B bond collinear with *x* axis. [b] Same bond distances as in ref 20 except symmetry assumed to be D_{2d}. [c] Structural data taken from ref 22b. [d] Same bond distances as in ref 22b except symmetry assumed to be D_{2h}. [e] See text and Table I. [f] Calculated from the following data: $\Delta H_f(B) = 139.2$, $\Delta H_f(F) = 19.0$, $\Delta H_f(B_2F_4) = -342.0$. All values in kcal/mole at 298 °K. [g] Energy difference between planar (D_{2h}) and staggered (D_{2d}) conformations. [h] See eq 9 for definition of orbital overlap population. [i] See eq 9 for definition of total overlap population.

Table III. Summary of the SCF–IO Results for B_2Cl_4

Property	Planar[a]	Staggered[b]	Exptl	Ref
IP, eV	8.71	8.49	...	
Total molecular energy, eV	−1454.69	−1454.32	...	*c*
ΔH_f, kcal/mole	−994.33	−985.72	−512.2	*d*
Barrier, kcal/mole	8.61[e]	1.8[f]		
	Orbital Overlap Population (OP)[g]			
$B(p_z)$–$B(p_z)$	0.1027	0.0540		
$B(p_y)$–$B(p_y)$	0.0249	0.0540		
$B(p_z)$–$Cl(p_z)$	0.1877	0.1927		
	Total Overlap Population (TOP)[h]			
B–B	1.0473	1.0286		
B–Cl	0.9014	0.8960		

[a] Reference 21. B–B bond collinear with *x* axis. [b] Bond distances same as in ref 21 except symmetry assumed to be D_{2d}. [c] See text and Table I. [d] Calculated from the following data: $\Delta H_f(B) = 139.2$, $\Delta H_f(Cl) = 28.95$, $\Delta H_f(B_2Cl_4) = -118.2$. All values in kcal/mole at 298 °K. [e] Energy difference between the planar (D_{2h}) and staggered (D_{2d}) conformations. [f] Reference 22a. [g] See eq 9 for definition of orbital overlap population. [h] See eq 8 for definition of total overlap population.

were evaluated by the Wolfsberg–Helmholtz approximation[19] with $K = 1.75$.

$$H_{uv} = 0.5K(H_{uu} + H_{vv})S_{uv} \tag{11}$$

Each of the above methods employs a valence atomic orbital basis set of Slater-type orbitals and assumes that the inner-shell electrons constitute a nonpolarizible core. The atomic orbital basis sets consisted of a 1s orbital for H, 2s and 2p orbitals for B, N, and F, and 3s and 3p orbitals for P and Cl. The orbital exponents of the 1s, 2s, 2p, 3s, and 3p functions were calculated by Slater's rules in the usual manner.

The sources of the structural data used in these calculations are indicated in the appropriate sections. In the absence of evidence to the contrary it was necessary to assume that the geometries of the AX_2 groups do not change upon rotation around the A–A bond of A_2X_4 molecules. See Table I for a summary of structural data.

Results and Discussion

At the outset it is well to point out that attempts to predict stable conformations and rotational barriers based solely on energetic considerations could be somewhat hazardous because such conclusions would depend on the differences of relatively large numbers. The approach taken here, therefore, is one of utilizing as many criteria of stability as possible. Thus, calculated ionization potentials, dipole moments, and nmr coupling constants of A_2X_4 molecules have been compared with the experimental values when these data were applicable or available. The nature of the bonding in each of the possible conformers has also been considered in assessing conformational preferences.

(a) Diboron Tetrahalides. The diboron tetrahalides are of interest because their conformations vary with the molecular state. Thus in the crystalline state both B_2F_4[20] and B_2Cl_4[21] adopt planar (D_{2h}) conformations. However, in the vapor state both electron diffraction[22] and vibrational spectroscopic studies[23] suggest that the staggered (D_{2d}) form represents a conformational energy

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minimum. The difference in energy between the D_{2h} and D_{2d} rotamers is probably quite small; hence free rotation around the B–B bond is probable at ambient temperature, particularly in the case of B_2F_4.

In our calculations on B_2F_4 we employed both the X-ray[20] and electron diffraction[22b] structural data. Essentially these data differ in the B–B bond length (1.67 *vs.* 1.75 Å). Only one calculation was necessary with B_2Cl_4 because both sets of structural data are in close agreement. (The electron diffraction range[22a] of 1.73–1.76 Å for the B–B bond distance encompasses the X-ray value[21] of 1.75 Å.) From the standpoint of total molecular energy (Tables II and III) the planar (D_{2h}) conformation is the more stable for both B_2F_4 and B_2Cl_4. Lengthening the B–B bond of B_2F_4 to the distance determined by electron diffraction[22b] diminishes the energy difference between the D_{2h} and D_{2d} models, but the former remains the more stable. On the basis of the present study the only way in which the D_{2d} model of B_2F_4 becomes favored energetically is if this conformer has a shorter B–B bond distance than the planar species. In any event, the energy differences between the D_{2d} and D_{2h} conformers is small for both B_2F_4 and B_2Cl_4. Further, the calculated heats of formation of both conformers of B_2F_4 and B_2Cl_4 are somewhat larger than the observed values (Tables II and III). Consequently the computed rotational barriers may also be overestimated.

Looking at the bonding in the B–B bond of the diboron tetrahalides (Tables II and III), it is evident that in both cases the planar model is stabilized by an appreciable π-type interaction between a $2p_z$ orbital on each boron atom. As expected the orbital overlap population, $P_{p_zp_z}$, decreases by approximately 50% upon rotation of one BX_2 group by 90°. The corresponding $P_{p_yp_y}$ orbital overlap population is smaller than the $P_{p_zp_z}$ overlap population in the D_{2h} conformer, but becomes equal to the latter in the D_{2d} conformer as demanded by symmetry considerations. For both rotamers of B_2F_4 and B_2Cl_4 the B–B σ bond is a combination of 2s–2s, 2s–$2p_x$, and $2p_x$–$2p_x$ interactions, and the total overlap population (TOP) between the two boron atoms remains essentially constant upon rotation. The boron–halogen bond comprises a σ contribution resulting from 2s(B)–*n*s(halogen), 2s(B)–*n*p_x(halogen), 2s(B)–*n*p_y(halogen), $2p_x$(B)–*n*p_x(halogen), and $2p_x$(B)–$2p_y$(halogen) interactions, and a π bond which results from a $2p_z$(B)–*n*p_z(halogen) interaction. As anticipated neither the σ bonding nor the π bonding in the boron–halogen bond is affected by rotation around the B–B bond. Although the $2p_z$(B)–$3p_z$(Cl) overlap population is larger than the $2p_z$(B)–$2p_z$(F) overlap population, the ratio of π to σ overlap is larger for the B–F bonds. Cotton and Leto's calculations[24] on the boron trihalides reveal a similar trend.

(b) Hydrazine. The conformation of hydrazine also appears to depend upon the molecular state. Thus in the solid state Collin and Lipscomb[25] concluded that N_2H_4 has either the eclipsed (C_{2v}) or a semieclipsed (C_2) conformation. A similar conclusion was reached on the basis of a neutron diffraction experiment.[26] Electron diffraction,[27] microwave,[28] and vibrational spectroscopic[29] experiments on hydrazine indicate that in the vapor phase the *gauche* (C_2) conformation represents a conformational energy minimum. The observation of a permanent dipole moment for both liquid[30] and gaseous[31] hydrazine precludes the exclusively *trans* conformation in these states. The possibility of an equilibrium between the *trans* and *gauche* rotamers has been discussed by Wagner and Bulgozdy[32] on the basis of significant changes in the ir and Raman spectra.

In the present sets of calculations, which are based on the structural data of Morino, Ijima, and Murata,[27b] the total energies (Table IV) indicate that the order of conformational stability is *gauche* > *cis* > *trans*.[33] The computed *cis* and *trans* barriers fall in the ranges 1.0–3.6

Table IV. Calculated Total Energies (eV) and Rotational Barriers (kcal/mol) for A_2X_4 Molecules

	SCF-IO	SCF-CNDO/2	EHT
	N_2H_4[a]		
gauche	−480.2003	−785.6388	−260.8404
cis	−480.0438	−785.5943	−260.7854
trans	−479.9438	−785.4268	−260.7091
cis barrier	3.6090	1.0262	1.2684
trans barrier	5.9151	4.8889	3.0279
	N_2F_4[a]		
gauche	−2322.3207	−3697.9151	−916.0799
cis	−2321.4262	−3697.9060	−915.9566
trans	−2320.6108	−3697.7477	−915.7474
cis barrier	20.6281	0.2075	2.8434
trans barrier	39.4320	3.8604	7.6678
	P_2H_4[a]		
gauche	−369.2003	−599.0945	−211.3228
cis	− 369.1451	−599.0544	−211.2426
trans	−368.8985	−599.1002	−211.1118
cis barrier	1.2730	. . .	1.8495
trans barrier	6.9598	. . .	4.8659
	P_2F_4[a]		
gauche	−2192.5834	−3523.4288	−876.9551
cis	−2191.5069	−3523.4176	−876.7566
trans	−2191.2140	−3523.2598	−876.6662
cis barrier	24.8252	0.2583	4.5776
trans barrier	31.5797	3.8973	6.6623

[a] See Tables V–VIII for structural data used in these calculations. [b] Total molecular energy; see ref 9. [c] Total molecular energy, see ref 15. [d] Total electronic energy; see ref 17.

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(33) The same conclusion is reached on the basis of charge-iterated extended Hückel calculations. Using the method of P. C. Van Der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966), we calculate the *cis* and *trans* barriers of hydrazine to be 4.81 and 5.19 kcal/mole, respectively.

Table V. Summary of the SCF–IO Results for the Rotamers of N_2H_4

Property	*gauche*[a]	*trans*[b]	*cis*[c]	Exptl
IP, eV	8.87	7.81	8.06	9.56,[d] 9.00[e]
Total molecular energy, eV	−480.2003	−479.9438	−480.0438	*f*
ΔH_f, kcal	−805.585	−799.671	−801.975	−411.621[g]
$J_{^{14}N-^{1}H}$, Hz[h]	+27.92	+27.56	+27.64	...
$J_{^{1}H-N-^{1}H}$, Hz	−15.07	−14.74	−14.58	...
μ, D	1.794	0	2.099	1.92[i] 1.75[j]
Orbital Overlap Population[k]				
N(p_z)–N′(p_z)	−0.0330	−0.0471	−0.0440	
N(p_y)–N′(p_y)	−0.0170	−0.0265	−0.0286	
Total Overlap Population[l]				
N–N′ TOP	0.6265	0.6021	0.6047	
N–H TOP	0.7634	0.7631	0.7655	

[a] Structural data taken from ref 27b. N–N bond collinear with *x* axis. [b] Same bond distances and bond angles as ref 27b but C_{2h} molecular symmetry. [c] Same bond distances and bond angles as ref 27b but C_{2v} molecular symmetry. [d] F. I. Vilesov, *Dokl. Akad. Nauk SSSR*, **132**, 632 (1960). [e] V. H. Dibeler, J. L. Franklin, and R. M. Reese, *J. Am. Chem. Soc.*, **81**, 68 (1959). [f] See text and Table I. [g] Calculated from the following data: $\Delta H_f(N) = 112.981$; $\Delta H_f(H) = 52.1$; $\Delta H_f(N_2H_4) = +22.74$. All values in kcal/mole at 298 °K. [h] Calculations based on molecular orbital expression for the contact term: J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964). [i] Liquid-phase value; ref 30. [j] Vapor-phase value; ref 31. [k] See eq 9 for definition of orbital overlap population. [l] See eq 8 for definition of total overlap population.

Table VI. Summary of the SCF–IO Results for the Rotamers of N_2F_4

Property	*gauche*[a]	Semieclipsed[b]	*trans*[c]	*cis*[d]	Exptl
IP, eV	7.79	7.39	5.98	6.36	12.04[e]
Total molecular energy, eV	−2322.3207	−2322.0409	−2320.6108	−2321.4262	*f*
$J_{^{14}N-^{19}F}$, Hz[g]	−99.92	−96.19	−100.58	−102.44	−117[h]
$J_{^{14}N-N-^{19}F}$, Hz	+11.26	+19.06	+8.84	+5.02	
μ, D	0.4046	0.0423	0	0.1956	0.26[i]
Orbital Overlap Population[j]					
N(p_z)–N′(p_z)	0.0493	0.0508	0.0114	0.0151	
N(p_y)–N′(p_y)	0.0448	0.0448	0.0231	0.0246	
Total Overlap Population[k]					
N–N′ TOP	0.8081	0.8052	0.7417	0.7563	
N–F TOP	0.4757	0.4724	0.4850	0.4845	

[a] Structural data taken from ref 36. N–N bond collinear with *x* axis. [b] Same bond distances and bond angles as ref 36 but C_2 molecular symmetry. [c] Same bond distances and bond angles as ref 36 but C_{2h} molecular symmetry. [d] Same bond distances and bond angles as ref 36 but C_{2v} molecular symmetry. [e] Reference 41. [f] See text and Table I. [g] Calculations based on molecular orbital expression for the contact term: J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964). [h] R. Ettinger and C. B. Colburn, *Inorg. Chem.*, **2**, 1312 (1963). [i] Reference 36. [j] See eq 9 for definition of orbital overlap population. [k] See eq 8 for definition of total overlap population.

and 3.0–5.9 kcal/mole, respectively. These may be compared with the experimental value[28] of 3.15 kcal/mole and the *ab initio* caclulated values[3] of 11.0–11.9 kcal/mole for the *cis* barrier and 3.7–6.2 kcal/mole for the *trans* barrier. Unfortunately the experimental (microwave) value[28] is of little value because it is based on the assumption that both barriers are equal. As already pointed out by Veillard,[3a] the *ab initio* theoretical barriers are probably too high; hence the values calculated here seem to be reasonable.

The ionization potentials, nuclear spin coupling constants, and dipole moments which were computed by the SCF–IO method are presented in Table V. The calculated ionization potential and dipole moment for the *gauche* conformer are closest to the experimental values, thus supporting the assignment of this isomer as the most stable. In each calculation the highest filled molecular orbital has a high % 2p(N) character, thus corresponding to the usual idea of a lone pair. There do not appear to be any nmr coupling constant data on N_2H_4 presumably due to inversional and rotational averaging and ^{14}N quadrupolar relaxation effects.[34] The order of conformational stability *gauche* > *cis* > *trans*, which is indicated in the present study, contrasts both with the *ab initio* theoretical order[3] *gauche* > *trans* > *cis* and with simple electrostatic considerations[35] which would presumably predict the order *trans* > *gauche* > *cis*. In our calculations the reason for the order of stability *gauche* > *cis* > *trans* is related to a combination of σ-bonding and π-antibonding factors. Thus, *e.g.*, in the SCF–IO calculations (Table V), it can

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(34) J. R. Cook and K. Schug, *J. Am. Chem. Soc.*, **86**, 4271 (1964), report that the ^1H nmr spectrum of N_2H_4 consists of a singlet at ambient temperature.

(35) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963).

Table VII. Summary of the SCF–IO Results for the Rotamers of P_2H_4

Property	*gauche*[a]	*trans*[a]	*cis*[a]	Exptl
IP, eV	9.20	8.44	8.91	. . .
Total molecular energy, eV	−369.2003	−368.8985	−369.1451	*b*
ΔH_f, kcal/mole	−578.6281	−571.6684	−577.3551	−364.58[c]
$J_{^{31}P-^{31}P}$, Hz[d]	−53.50	+169.02	−84.62	−108.2[e]
$J_{^{31}P-^{1}H}$, Hz	+168.99	+160.00	+167.60	+186.2[e]
$J_{^{1}H-P-^{1}H}$, Hz	−13.37	−12.70	−13.06	−12.0[e]
μ, D	3.22	0	3.54	. . .
Orbital Overlap Population[f]				
$P(p_z)$–$P'(p_z)$	−0.0118	−0.0268	−0.0269	
$P(p_y)$–$P'(p_y)$	−0.0243	−0.0242	−0.0252	
Total Overlap Population[g]				
P–P′ TOP	0.6705	0.6555	0.6548	
P–H TOP	0.7958	0.7905	0.7953	

[a] Structural data assumed: P–P = 2.21 Å, P–H = 1.42 Å: ∠PPH = 100°, ∠HPH = 92°. P–P bond collinear with *x* axis for all three conformers. [b] See text and Table I. [c] Calculated from the following data: $\Delta H_f(P) = 75.59$; $\Delta H_f(H) = 52.1$; $\Delta H_f(P_2H_4) = +5.0$. All values in kcal/mole at 298 °K. [d] Calculations based for molecular orbital expression for the contact term: J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964). [e] Reference 46. [f] See eq 9 for definition of orbital overlap population. [g] See eq 8 for definition of total overlap population.

Table VIII. Summary of the SCF–IO Results for the Rotamers of P_2F_4

Property	*gauche*[a]	*trans*[a]	*cis*[a]	Exptl
IP, eV	7.02	5.43	5.89	. . .
Total molecular energy, eV	−2192.5834	−2191.2140	−2191.5069	*b*
$J_{^{31}P-^{19}F}$, Hz[c]	−1188.90	−1160.77	−1250.73	−1198.5[d]
$J_{^{31}P-^{31}P}$, Hz	+217.09	+707.35	+212.16	+227.4[d]
$J_{^{31}P-P-^{19}F}$, Hz	+106.69	+183.98	+104.76	+67.5[d]
μ, D	0.216	0	0.169	
Orbital Overlap Population[e]				
$P(p_z)$–$P'(p_z)$	0.0635	0.0172	0.0191	
$P(p_y)$–$P'(p_y)$	0.0599	0.0243	0.0253	
Total Overlap Population[f]				
P–P′ TOP	0.9228	0.8305	0.8480	
P–F TOP	0.4423	0.4343	0.4337	

[a] Structural data assumed: P–P = 2.21 Å, P–F = 1.57 Å; ∠PPF = 110°, ∠FPF = 110°. P–P bond collinear with *x* axis for all three conformers. [b] See text and Table I. [c] Calculations based on molecular orbital expression for the contact term: J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964). [d] Reference 40. [e] See eq 9 for definition of orbital overlap population. [f] See eq 8 for definition of total overlap population.

be seen that there are negative orbital overlap populations for the $2p_z(N)$–$2p_z(N')$ and $2p_y(N)$–$2p_y(N')$ interactions indicating an antibonding π interaction between the nitrogen atoms. The antibonding π character is largest for the *trans* conformer and smallest for the *gauche* conformer. The σ bonding between nitrogen atoms comprises $2s(N)$–$2s(N')$, $2s(N)$–$2p_x(N')$, and $2p_x(N)$–$2p_x(N')$ interactions. Significantly, the total overlap population for σ bonding is also in the order *gauche* > *cis* > *trans*. As expected the N–H bonding, which is restricted to a σ-type interaction, is not appreciably different for each of the rotamers.

(c) Tetrafluorohydrazine. There still appears to be some doubt concerning the structure of tetrafluorohydrazine. The microwave data,[36] upon which our calculations are based, were interpreted on the basis of C_2 symmetry, although the *trans* conformer could not be excluded. The initial vibrational spectroscopic data[37] were assigned on the basis of the *gauche* conformation. However, in a more recent Raman and ir study,[38] it was concluded that the *gauche* and *trans* conformers are in equilibrium at both ambient and low temperatures. A similar conclusion had been reached earlier on the basis of a low-temperature ^{19}F nmr investigation.[39] In contrast to the latter, Bohn and Bauer's electron diffraction study[40] excludes the *trans* isomer as the dominant structure and suggests that another explanation must be found for the observed single strong line ascribed to this species in the nmr study.

On the basis of all three methods of calculation we

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(36) D. R. Lide and D. R. Mann, *J. Chem. Phys.*, **31**, 1129 (1959).

(37) (a) Yu. I. Kotov and V. M. Tatenskii, *Opt. i Spektroskopiya*, **14**, 443 (1963); (b) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958); (c) J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 1877 (1963); (d) E. N. Moskvitina, *et al.*, *Opt. i Spektroskopiya*, **16**, 768 (1964); *Tr. Komis po Spektroskopii Akad. Nauk. SSSR*, **3**, 197 (1964).

(38) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **48**, 3216 (1968).

(39) C. B. Colburn, F. A. Johnson, and C. Haney, *ibid.*, **43**, 4526 (1965).

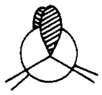
(40) R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 304 (1967).

reach a very similar conclusion regarding the total energies of the three conformers (Table IV) to that described previously for hydrazine, namely an order of conformation stability *gauche* > *cis* > *trans*. An SCF–IO calculation of the total molecular energy of the semieclipsed (C_2) form (Table VI) indicates that this species is of a stability intermediate between that of the *cis* and *gauche* rotamers. From the overlap population aspect it is also apparent (Table VI) that the total overlap population between the two nitrogen atoms of N_2F_4 is in the order *gauche* > *cis* > *trans*, thus supporting the above conclusion based on total energies. However, in contrast to N_2H_4, the SCF–IO calculations indicate that the π-type contributions from the $2p_z(N)$–$2p_z(N')$ and $2p_y(N)$–$2p_y(N')$ interactions are slightly positive.

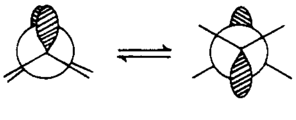
As expected the total overlap populations for the N–F bonds are essentially the same for each of the rotamers. This similarity persists in the calculated ^{14}N–^{19}F nuclear spin coupling constants. There is a relatively poor agreement between the three methods regarding the calculated *cis* and *trans* barriers in N_2F_4 (Table IV). Unfortunately there are no experimental data pertaining to either of these barriers, but it is probable that the SCF–IO values are somewhat high. In the microwave study[36] it was suggested that the rotational barrier is >3 kcal/mole.

The calculated ionization potentials are all consistently smaller than the observed value of 12.04 eV.[41] Our calculated value for the ionization potential of NF_3 was also too small. The problem with the fluorinated species may arise from the neglect of one-center exchange integrals in our treatment.[42] In any event, it is of interest to note that the ionization potential computed for the *gauche* conformer is nearest to the experimental value. On the other hand, the calculated and observed dipole moment agreement is best for the *cis* species although an equilibrium mixture of conformers is obviously possible.

Summarizing the findings on N_2F_4 it can be said that there is no support for the *trans* isomer being the most stable. This would seem to contradict the conclusions of the low-temperature ^{19}F nmr experiments on this compound, where the assignment of the ^{19}F nmr singlet to the *trans* conformation is an unstated assumption.[39] The authors do not appear to consider a further two possible causes of equivalence in the ^{19}F nmr, namely (a) the *cis* conformation



and (b) rapid interconversion between the *cis* and *trans* forms *via* inversion at one nitrogen atom



(d) Diphosphine and Tetrafluorodiphosphine.[41] Considerably less structural information is available on these molecules; hence it was necessary to assume the structural data on which these calculations are based (see Tables VII and VIII). Vibrational spectroscopic data favor the *gauche* and *trans* conformations for P_2H_4[43,44] and P_2F_4,[45] respectively. The nmr data for P_2H_4 were analyzed in terms of (assumed) rapid rotation about the P–P bond and consequent C_{2v} symmetry.[46] In the nmr study of P_2F_4[47] the spectral analysis was carried out on the assumption that the molecule possessed the *trans* conformation.

With the exception of the SCF–CNDO/2 calculations on P_2H_4, the computed total energies (Table IV) suggest that the order of conformational stability is *gauche* > *cis* > *trans* for both P_2H_4 and P_2F_4. For P_2H_4 the SCF–IO and EHT calculations are in reasonable agreement regarding the *cis* and *trans* barriers and indicate that the rotational barriers are not very different from those in hydrazine. The three methods do not agree with respect to the rotational barriers in P_2F_4. As in the case of N_2F_4 the SCF–IO computed barriers are probably somewhat high.

Very recently Finer and Harris[48] have shown that the sign of the P–P coupling constant is dependent upon the valence state of phosphorus and also upon the substituent electronegativity and bulk. Of special concern to the present problem was the suggestion that the ^{31}P–^{31}P coupling constant is positive in P_2F_4 and negative in P_2H_4. Accepting this suggestion the computed nuclear spin coupling constant data (Table VII) for P_2H_4 would seem to rule out the *trans* conformation but do not permit a distinction to be made between the *cis* and *gauche* models. Similarly in P_2F_4 (Table VIII) the *trans* model would not appear to be favored on account of the substantially larger calculated magnitude of the ^{31}P–^{31}P coupling constant. So far as we are aware, there are no ionization potential data or dipole moment data available for either P_2H_4 or P_2F_4.

Essentially the same comments could be made regarding the bonding situation in P_2H_4 and P_2F_4 as have been made previously for the corresponding nitrogen compounds, namely that the total overlap populations ($\sigma + \pi$) for the P–P bonds in both molecules are in the order *gauche* > *cis* > *trans*.

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