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A Population Analysis of the Bonding in N_2O_4, B_2Cl_4, B_2F_4, C_2H_4 and C_3H_4

EMMETT B. MOORE jr.

Boeing Scientific Research Laboratories, Seattle, Washington

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Population matrices have been calculated from molecular orbital wave functions of N_2O_4, B_2Cl_4, and B_2F_4 in order to understand further the bonding in these molecules which are isoelectronic in valence electrons but different in structure. C_2H_4 and C_3H_4 have been included in this study as check cases.

Des matrices d'occupation ont été calculées à partir des orbitales moléculaires de N_2O_4, B_2Cl_4 et B_2F_4, afin de comprendre plus profondément la liaison dans ces molécules, qui sont isoélectroniques par leurs électrons de valence, mais qui n'ont pas la même structure. C_2H_4 et C_3H_4 sont considérés dans cette étude à titre de vérification.

Ausgehend von Molekülorbitalen werden Besetzungsmatrizen für N_2O_4, B_2Cl_4 und B_2F_4 berechnet, um die Bindung in diesen Molekülen, die in den Valenzelektronen isoelektronisch sind, aber unterschiedliche Strukturen aufweisen, besser zu verstehen. C_2H_4 und C_3H_4 sind in dieser Untersuchung als Prüffälle eingeschlossen.

Introduction

Electron diffraction [*1*] and spectroscopic [*2*] studies show that N_2O_4 exists in the eclipsed (planar) form in the gas phase while similar electron diffraction [*3, 4, 5*] and spectroscopic [*6, 7*] studies show that B_2Cl_4 exists in the staggered form in the gas phase (Fig. 1). Also the barrier to internal rotation in N_2O_4 has been determined to be 2.9 kcal/mole by spectroscopic means [*2*], while the barrier in B_2Cl_4 has been determined to be 1.7 ± 0.6 kcal/mole by spectroscopic means [*7*] and 1.8 kcal/mole at room temperature by electron diffraction means [*8*]. These results raise the question as to whether or not they can be interpreted by simple quantum theory. In an earlier investigation [*9*] we have shown that extended-Hückel theory [*10*] energies describe correctly the more stable of the two forms of B_2Cl_4 and N_2O_4 and give reasonable values of the internal rotation barriers. Recent work [*11, 12*] however suggests that extended-Hückel theory (EHT) wave functions may be regarded as much better approximations to self-consistent-field (SCF) wave functions than EHT molecular energies may be regarded as approximations to SCF molecular energies. Accordingly we have reopened our investigation and in this paper we examine population matrices calculated from EHT wave functions in order to gain further insight into the bonding in the two forms of N_2O_4, B_2Cl_4 and B_2F_4. We also consider C_2H_4 and C_3H_4 as check cases.

Molecular Coordinates

The staggered (D_{2d}) molecular conformation and coordinate system are shown in Fig. 1. The planar conformation is obtained by rotating the $Y_1 - A_1 - Y_2$

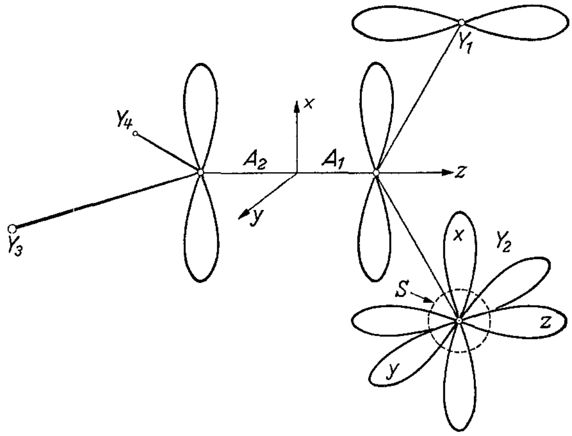

Fig. 1. Outline of the staggered (D_{2d}) form of A_2Y_4 showing some of the valence atomic orbitals used in this study. The 1s orbital only was used for H (not shown), the 2s and 2p orbitals were used for B, C, N, O, and F, and the 3s and 3p were used for Cl, as shown on atom Y_2. Not all of the atomic orbitals are shown on every atom for clarity. The π interactions between A_1 and A_2 are $p_x - p_x$ and $p_y - p_y$. The $A_2 - Y_1$ interaction is between the p_x orbital on A_2 and the p_z orbital on Y_1

group by 90° about the $A_1 - A_2$ axis. N_2O_4 [*1, 2*] and C_2H_4 [*13*] are known to have D_{2h} symmetry in the gas phase while B_2Cl_4 [*3—7*] and C_3H_4 [*14*] are known to have D_{2d} symmetry in the gas phase (the three carbon atoms in C_3H_4 form a linear chain along the rotation axis). The coordinates for each molecule are listed in Tab. 1. The structure of B_2F_4 in the gas phase has not yet been published, so the coordinates in Tab. 1 are those of the planar form in the crystal [*15*].

Table 1. *Atomic coordinates (in Å) from Ref.* [*1, 13, 15, 5, 14*] *respectively. Coordinates of the unlisted atoms may be derived by symmetry and reference to Fig. 1*

		x	*y*	*z*
N_2O_4	N_1	0.0	0.0	0.875000
(D_{2h})	O_1	0.0	−1.084985	1.338905
C_2H_4	C_1	0.0	0.0	0.668450
(D_{2h})	H_1	0.0	−0.948319	1.231744
B_2F_4	B_1	0.0	0.0	0.835000
(D_{2h})	F_1	0.0	−1.143154	1.495000
B_2Cl_4	B_1	0.0	0.0	0.839500
(D_{2d})	Cl_1	1.507500	0.0	1.734219
C_3H_4	C_1	0.0	0.0	1.308800
(D_{2d})	C_2	0.0	0.0	0.0
	H_1	0.909800	0.0	1.866300

Method of Calculation

We used HOFFMANN's EHT program [*10*] which we modified to include 3s and 3p atomic orbitals [*16*]. Besides computing the molecular orbitals (MO's) and

Table 2. *Slater exponentials and valence state ionization energies*

Atom	Orbital	μ	$H_{\alpha\alpha}$
H	$1s$	1.000	−13.60 eV
B	$2s$	1.300	−15.16
B	$2p$	1.300	− 8.31
C	$2s$	1.625	−21.20
C	$2p$	1.625	−10.77
N	$2s$	1.950	−25.56
N	$2p$	1.950	−13.19
O	$2s$	2.275	−32.33
O	$2p$	2.275	−15.80
F	$2s$	2.600	−40.12
F	$2p$	2.600	−18.65
Cl	$3s$	2.033	−25.27
Cl	$3p$	2.033	−13.69

their energies this program also computes the population matrix and charge distribution from the filled MO's. Each population matrix element may be regarded as a relative bond order between two atomic orbitals which may be compared within a molecule or between two conformations of the same molecule.

For the diagonal Hamiltonian matrix elements we used BASCH, VISTE and GRAY's [*17*] valence orbital ionization energies, for the off-diagonal Hamiltonian matrix elements we used the WOLFSBERG-HELMHOLZ approximation [*18*] with a value of 2.0 for the constant, and for the overlap integrals we used the usual values of the Slater exponential factors (Tab. 2).

Results

In spite of the crudeness of the EHT molecular energy calculation, it is gratifying that the energies accurately describe the stable forms of C_2H_4, C_3H_4, N_2O_4, and B_2Cl_4 and give reasonable values of the barrier to internal rotation as well (Tab. 3). In the case of B_2F_4, the energy calculation predicts that the two ends of the molecule rotate virtually freely about the $B_1 - B_2$ axis. The differences between the barrier energies of N_2O_4 and B_2Cl_4 in this study and our previous one [*9*] are due to differences in the atomic coordinates and differences in valence orbital ionization energies.

Table 3. *Barriers to internal rotation*

Molecule	Stable Form		Barrier	
	Theory	Expt.	Theory kcal/mole	Expt. kcal/mole
C_2H_4	D_{2h}	D_{2h}	101.7	?
C_3H_4	D_{2d}	D_{2d}	36.5	?
N_2O_4	D_{2h}	D_{2h}	2.11	2.9
B_2Cl_4	D_{2d}	D_{2d}	1.67	1.7 − 1.8
B_2F_4	D_{2d}	D_{2d}	0.003	?

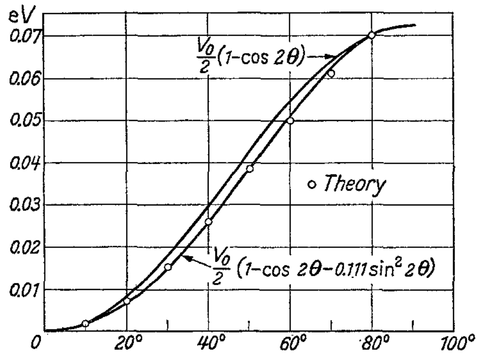

Fig. 2. Experimental ($0.5\ V_0(1-\cos 2\theta)$) and theoretical ($0.5\ V_0(1-\cos 2\theta - 0.111 \sin^2 2\theta)$) shape of the barrier to internal rotation in B_2Cl_4. The circles are the calculated theoretical values

We also calculated the shape of the barrier in B_2Cl_4 to compare with HEDBERG's experimentally determined curve [8]. He found the shape of the barrier to be given by $V = 0.5\ V_0\ (1 - \cos 2\theta)$ from electron diffraction data. Our calculated curve (Fig. 2) agrees very closely with this equation but contains a small second order correction: $V = 0.5\ V_0\ (1 - \cos 2\theta - 0.111 \sin^2 2\theta)$.

The first thing we noticed when we began our examination of the MO wave functions and population matrices was that the staggered form of C_2H_4 is orbitally degenerate. This means that C_2H_4 would be expected to distort away from D_{2d} symmetry according to the Jahn-Teller theorem [19], which says that any non-linear, orbitally degenerate array of atoms will distort in such a fashion as to remove the degeneracy. A cursory survey of the literature failed to reveal that this fact has been pointed out before. The D_{2d} forms of C_3H_4, N_2O_4, B_2Cl_4, and N_2O_4 are not orbitally degenerate.

In studying bonding MO population matrix elements one must decide either to look at just the positive off-diagonal elements, which may be considered to represent bond strengths, or to include the negative elements as well, which presumably represent anti-bonding situations. The positive elements may take any value between zero and about 1.0 whereas the negative values are nearly always close to zero. In either case the results are the same in this study so we have chosen the esthetically more pleasing course of disregarding the small negative off-diagonal population matrix elements (i.e. setting them equal to zero).

In Tab. 4 are shown the total $A_1 - Y_1$ populations, which are the sums of the individual AO pair populations for the two atoms. Also shown are the $A_1 - A_2$

Table 4. $A_1 - A_2$ *and* $A_1 - Y_1$ *populations (positive matrix elements only)*

	D_{2h}				D_{2d}			
	$A_1 - Y_1$	$A_1 - A_2$ σ	$A_1 - A_2$ π_x	$A_1 - A_2$ π_y	$A_1 - Y_1$	$A_1 - A_2$ σ	$A_1 - A_2$ π_x	$A_1 - A_2$ π_y
C_2H_4	.8236	.8968	.4269	0	.7853	.8943	.0359	.0359
C_3H_4	.7654	.8998	.2842	.1233	.7968	.8998	.0382	.4265
N_2O_4	.9821	.4331	.0057	0	.9798	.4355	.0005	.0005
B_2Cl_4	.8390	.8672	.0180	0	.8315	.8667	.0019	.0019
B_2F_4	.5051	.8845	0	0	.5050	.8846	0	0

Table 5. *Non-adjacent atom and* $A_1 - A_2$ π *populations in* N_2O_4, B_2Cl_4 *and* B_2F_4 *(positive matrix elements only). There are four* $A_2 - Y_1$ *interactions and two each* $Y_1 - Y_3$ *and* $Y_1 - Y_4$ *interactions in each molecule*

	D_{2h}				D_{2d}			
	π	$A_2 - Y_1$	$Y_1 - Y_3$ $Y_1 - Y_4$	Total	π	$A_2 - Y_1$	$Y_1 - Y_3$ $Y_1 - Y_4$	Total
N_2O_4	.0057	0	.0040	.0097	.0010	.0044	.0012	.0066
B_2Cl_4	.0180	.0036	.0002	.0218	.0038	.0248	0	.0286
B_2F_4	0	.0004	.0002	.0006	0	.0040	0	.0040

populations broken down into σ- and π-contributions. The σ's are the sums of the $s - s$, $s - p_z$, and $p_z - p_z$ interactions, while π_x and π_y represent the $p_x - p_x$ and $p_y - p_y$ interactions respectively. The p_x orbitals are perpendicular to the molecular plane in D_{2h} symmetry while the p_y orbitals lie in the molecular plane. It can be easily seen that the π_x (out of plane) bond stabilizes the planar form of C_2H_4 as expected. This same out of plane bond stabilizes the staggered form of C_3H_4 although in this case there are two out of plane carbon-carbon π-bonds, one in each half of the molecule, which are rotated 90° with respect to one another.

It would appear from Tab. 4 that both N_2O_4 and B_2Cl_4 would be stable in the planar forms while B_2F_4 would rotate freely. It is necessary, however, to examine the situation somewhat further since the π-populations are so small. In fact there are appreciable contributions from interactions between non-adjacent atoms which alter the situation for B_2Cl_4 and B_2F_4 but do not change the situation for N_2O_4. These interactions are shown in Tab. 5.

In planar N_2O_4 the $N_1 - N_2$ π interaction is very weak but still strong enough to over-ride any bonding between non-adjacent atoms in the staggered form and keep the planar form stable. In planar B_2Cl_4 the $B_1 - B_2$ π-bond is stronger than the same bond in N_2O_4, yet it is dominated by interactions between non-adjacent boron and chlorine atoms in the staggered form. Specifically the p_x orbital on B_2 bonds with the p_z orbitals on Cl_1 and Cl_2 strongly enough to stabilize the staggered conformation of B_2Cl_4 over the planar one (Fig. 1). The same situation is present to a very small extent in B_2F_4 suggesting that the staggered form is somewhat more stable than the planar form, a result which is in agreement with spectroscopic evidence [*20*].

In conclusion, both the population matrices and the molecular energy differences from extended-Hückel theory yield the quantum mechanical description, in agreement with experiment, that C_2H_4 and N_2O_4 are stable in the gas phase in the planar form while C_3H_4 and B_2Cl_4 are stable in the staggered form. B_2F_4 is predicted to be nearly freely rotating although very slightly stable in the staggered form.

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Dr. E. B. MOORE jr.
Boeing Scientific Research Lab.
Seattle, Washington, USA