Theoret. chim. Acta (Berl.) 18, 258—260 (1970)

Extended Hückel Calculations on $n-v$ Addition Compounds

SHANTI A. KUDCHADKER and C. N. R. RAO
Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-16, India

Received May 20, 1970

Extended Hückel calculations are found to satisfactorily account for the various properties of the $n-v$ addition compounds.

Among the various types of electron donor-acceptor interactions, the interaction between n-donors (Lewis bases) and v-acceptors (Lewis acids) is associated with the largest energy [1, 2]. Thus, $n-v$ interaction is responsible for the formation of stable addition compounds such as BF_3 etherate. We wish to report the results of our molecular orbital calculations on a few $n-v$ addition compounds of BF_3 and BH_3 employing the extended Hückel approximation of Hoffmann [3]; Hoffmann [3] has reported some preliminary results on pyridine boranes, but detailed calculations (including potential energy curves) on a variety of these systems have not been carried out. We may note here that extended Hückel calculations have been quite successful in predicting the properties of hydrogen bonded systems [4–6].

We calculated [7] the total energies, E_T, of the addition compounds as functions of the boron-donor (B ... D) distances taking the other structural parameters from the literature [8–12]. In a few cases, we calculated the potential energy curves after minimizing E_T with respect to the B–F as well as the FBF angle, but the D_e did not vary significantly. For $BH_3 \cdot NH_3$, where only the B ... N distance has been reported [13], we minimized E_T with respect to the B–H distance assuming the angles to the tetrahedral. In our evaluation of the off-diagonal elements by the method of Wolfsberg and Helmholz [14] we have employed a K value of 1.75.

The important results from our calculations are summarized in the Table. The dissociation energies and the equilibrium B...D distances, R, obtained from the potential energy curves are in fair agreement with the experimental values; in BH_3–NH_3, however, the calculated B...N distance is somewhat longer. The results in the Table clearly indicate extensive donor-acceptor charge-transfer. The charge at the donor site decreases while that at fluorine (or hydrogen) increases on complex formation; the positive charge on boron decreases in all the cases except in $BF_3 \cdot O(CH_3)_2$ where it is essentially unaffected. An examination of the σ and π densities shows that the $\sigma(s, p_x)$ densities at the donor atoms decrease appreciably while the π densities are slightly reduced. There is an increase in the $\sigma(s, p_x)$ densities at the boron and the fluorine atoms in all the complexes except $BF_3 \cdot O(CH_3)_2$. In the etherate, the s density increases while the p_x density decreases; the p_x density at the donor oxygen is unaffected, Table. *Extended Hückel calculations on $n-v$ addition compounds*

Compound[a]	$R_{B\ldots D}$, Å		E_{min}	D_e (eV)		Charges[b]			Mulliken overlap Populations[b]	
	Calc.	Exp.	(eV)	Calc.	Exp.	B	F (or H)	D	B–F(H)	B ... D
$BF_3 \cdot O(CH_3)_2$ [8, 9]	1.75	1.50	− 971.698	0.35[c]	0.59 [15]	+2.327 (+2.309)	−0.823 (−0.770)	−0.958 (−1.132)	0.266 (0.345)	0.230
$BF_3 \cdot NH_3$ [10]	1.69	1.60	− 728.633	1.64	—	+2.081	−0.821	−0.615 (−1.034)	0.270	0.456
$BF_3 \cdot NCCH_3$ [11]	1.67	1.63	− 872.707	1.67	1.15 [16]	+2.061	−0.816	−0.646 (−1.064)	0.278	0.480
$BF_3 \cdot NC_5H_5$ [12]	1.60	1.53	−1117.656	2.32	2.0 [17]	+2.054	−0.829	−0.378 (−0.858)	0.255	0.559
$BH_3 \cdot NH_3$[d] [13]	1.90	1.60	− 246.640	0.45	—	+0.307 (+0.442)	−0.211 (−0.147)	−0.689 (−1.034)	0.788 (0.850)	0.295

[a] The reference shown next to the compound gives structural parameters.

[b] The values in parentheses refer to the charges or overlap populations in the parent acceptor or donor molecules.

[c] D_e was 0.5 eV when the B–F distance of 1.54 Å (obtained by minimizing E_T) was employed instead of the literature value of 1.43 Å.

[d] B–H distance (obtained by minimizing E_T) was 1.33 Å.

but the *s* density decreases. The π densities at the boron and fluorine atoms are slightly higher in the complexes. In the case of the pyridine and nitrile complexes, the σ densities at the carbon next to the donor site show an increase on complexation.

The Mulliken overlap population of the B–F (or B–H) bond shows a marked decrease in the complex. The overlap population of B ... D bonds are appreciable as expected in such strong addition compounds, the population being maximum in the strongest complex ($BF_3 \cdot$pyridine) and lowest in the weak complex, $BF_3 \cdot$etherate. The overlap populations of the bonds directly linked to the donor atoms are slightly greater in the addition compounds. In the pyridine complex, the C–N overlap population is also enhanced as noted earlier by Hoffmann [3].

The authors are thankful to the staff of the I.I.T. Kanpur Computer Centre for assistance with the IBM 7044 computer and to the U.S. National Bureau of Standards for a research grant under their Special International Programme.

References

1. Mulliken, R. S., Person, W. B.: Molecular complexes. New York: Wiley-Interscience 1969.
2. Rao, C. N. R., Murthy, A. S. N.: In: Spectroscopy in inorganic chemistry, ed. by C. N. R. Rao and J. R. Ferraro. New York: Academic Press 1970.
3. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963); **40**, 2474 (1964).
4. Adam, W., Grimison, A., Hoffman, R., de Ortiz, C. Z.: J. Amer. chem. Soc. **90**, 1509 (1968).
5. Murthy, A. S. N., Davis, R. E., Rao, C. N. R.: Theoret. chim. Acta (Berl.) **13**, 81 (1969).
6. — Bhat, S. N., Rao, C.N. R.: J. chem. Soc. (London) **1970**, 1251.
7. Hoffman, R.: Quantum Chemistry Program Exchange (QCPE 30), Bloomington, Indiana.
8. Buikis, U., Kasai, P. H., Myers, R. J.: J. chem. Physics **38**, 2753 (1963).
9. Bauer, S. H., Finlay, G. R., Laubengayer, A. W.: J. Amer. chem. Soc. **67**, 339 (1945).
10. Hoard, J. L., Geller, S., Cashin, W. M.: Acta crystallogr. **4**, 396 (1951).
11. Swansow, B., Shriver, D. F., Ibers, J. A.: Inorg. Chem. **8**, 2182 (1969).
12. Zvonkova, Z. V.: Kristallografiya **1**, 73 (1956).
13. Hughes, E. W.: J. Amer. chem. Soc. **78**, 502 (1956); Lippert, E. L., Lipscomb, W. L.: J. chem. Soc. 503 (1956).
14. Wolfsberg, M., Helmholz, I.: J. chem. Physics **20**, 837 (1952).
15. Brown, H. C., Adams, R. M.: J. Amer. chem. Soc. **64**, 2557 (1942).
16. Laubengayer, A. W., Sears, D. B.: J. Amer. chem. Soc. **67**, 164 (1945).
17. Lappert, M. F., Smith, J. K.: J. chem. Soc. (London) **1965**, 7102.

Professor Dr. C. N. R. Rao
Department of Chemistry
Indian Institute of Technology
Kanpur-16, India