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Theoretical study of the conformation of bis(1,4-difluorobenzene)vanadium

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Abstract

The conformation of bis(1,4-difluorobenzene)vanadium system is studied by the extended Hückel method. The dihedral angle between the two rings is calculated to be 58° in reasonable agreement with the observed value of 53°. The dominating factor for the conformation is the delocalization effect of the metal nonbonding orbital ($d_{x^2-y^2}$, d_{xy}) towards the vacant $d_{x^2-y^2}$-type and d_{xy}-type orbitals on the two rings. The interaction is maximised at 45°, for the two ring LUMO's, the d_{xy}-type orbitals, are able to interact independently with the metal $d_{x^2-y^2}$ and d_{xy} orbitals. In this work, the symmetries of the ring orbitals are referred to the axis system fixed on the ring.

Introduction

Radonovich and coworkers showed that the molecular structure of bis(1,4-difluorobenzene)vanadium(0) consists of a vanadium atom sandwiched between two parallel 1,4-difluorobenzene ligands in a D_2 symmetry [1]. One interesting feature of the structure is that the dihedral angle between fluorine atoms in the opposite rings is 53°. However, one would expect the most stable conformation to be a one with the dihedral angle about 90°, giving the largest fluorine–fluorine separation and hence the least steric interaction between the two rings. Radonovich et al. also reported some other bis(arene) complexes with bulky substituent such as trifluoromethyl group with which the dihedral angle is also much smaller than 90° [2].

Calculations

To obtain an understanding about these unexpected results, we have carried out a theoretical study for this system using the Extended Hückel method [3]. Our calculation indeed confirms the observed conformation. It appears that the dominating factor is the electronic interaction between the occupied metal e_2 set (d_{xy},

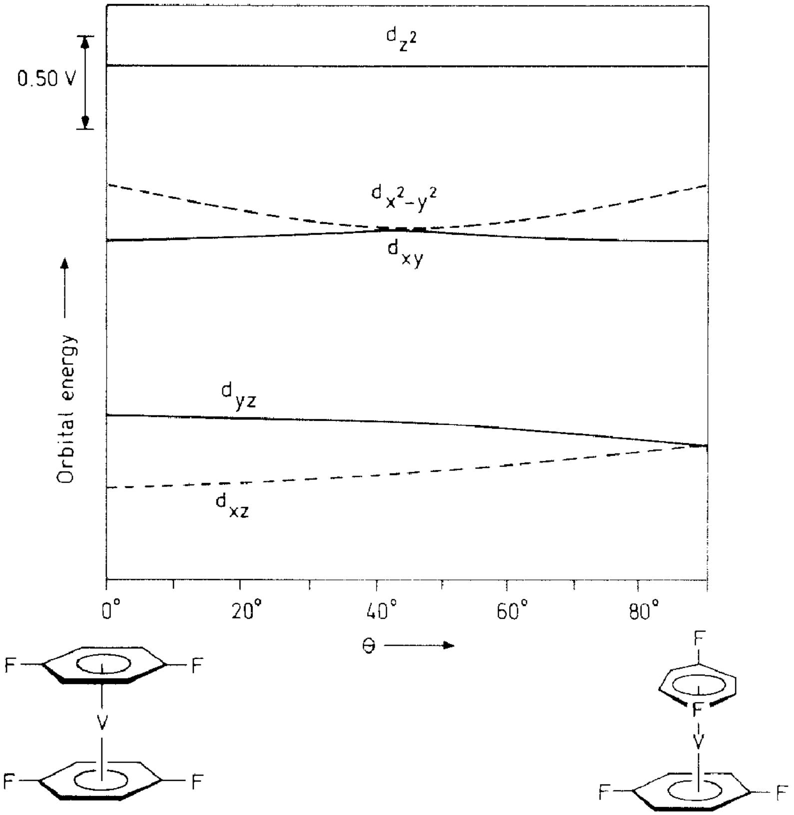

Fig. 1. The orbital energies (eV) as functions of the dihedral angle θ.

$d_{x^2-y^2}$) and the vacant e_2 set on the 1,4-difluorobenzene. The two e_2 π orbitals on the ring are labelled as $e_2(x^2-y^2)$ and $e_2(xy)$ to indicate good phase matching with the metal $d_{x^2-y^2}$ and d_{xy} when the ring is aligned with the two fluorine atoms along the y axis. In fact, the coordinate system for the ligand orbitals $e_2(x^2-y^2)$ and $e_2(xy)$ are referred to the x and y axis fixed on the ring and independent of the dihedral angle. Therefore the metal $d_{x^2-y^2}$ can overlap with the $e(x^2-y^2)$ of one ring and the $e(xy)$ of the other when the latter has a dihedral angle of 45° relative to the former.

Figure 1 shows the orbital energies for five high-lying orbitals as the functions of dihedral angle. Their characters are essentially d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz} and d_{xz}, respectively. The HOMO, d_{z^2}, is singly occupied for this 17 electron species. It is

Table 1

Net AO populations of vanadium 3*d* orbitals as functions of the dihedral angle θ

θ	0°	15°	30°	45°	60°	75°	90°
d_{z^2}	1.002	1.002	1.002	1.002	1.002	1.002	1.002
$d_{x^2-y^2}$	1.529	1.519	1.498	1.486	1.496	1.519	1.531
d_{xy}	1.447	1.458	1.478	1.486	1.475	1.458	1.450
d_{xz}	0.552	0.551	0.549	0.546	0.542	0.540	0.539
d_{yz}	0.526	0.526	0.529	0.532	0.536	0.538	0.539

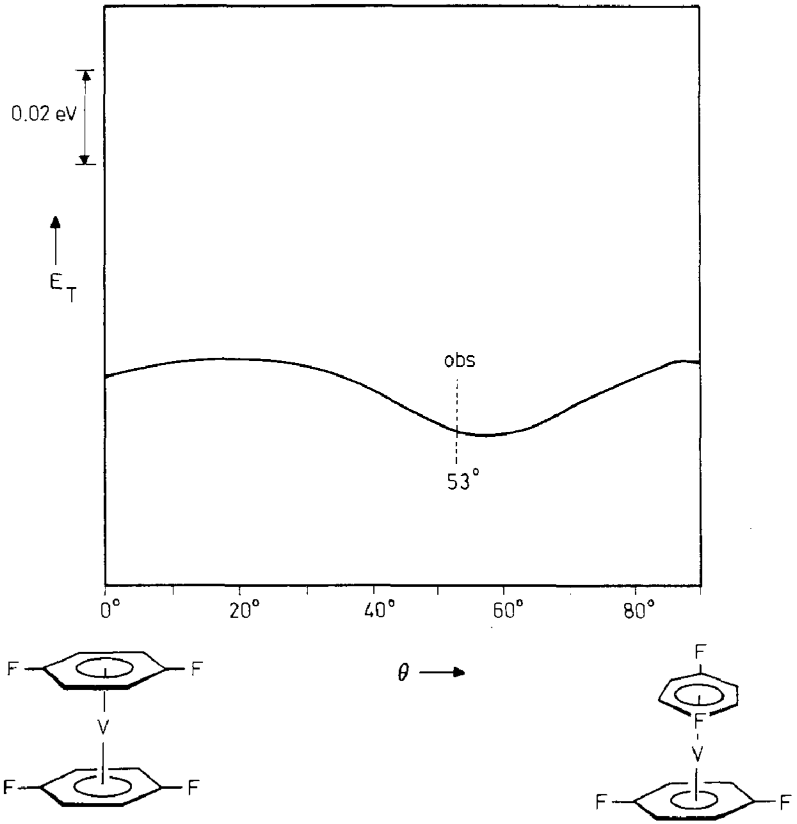

Fig. 2. The total energy (eV) as a function of the dihedral angle θ.

interesting to see that the $d_{x^2-y^2}$ orbital energy curve shows a similar behavior to that of the total energy depicted in Fig. 2. The latter gives the rotation barrier about 0.02 eV. Both of them show a minimum near 50°. This prompted us to study the behavior of this key orbital in more detail. In a pseudooctahedral field such as the one in the present work, d_{xz} and d_{yz} orbitals should be above $d_{x^2-y^2}$, d_{xy} and d_{z^2}. The two lower orbitals d_{yz} and d_{xz} here are in fact the bonding combinations of the e_1 difluorobenzene orbitals and d_{xz} and d_{yz}. These two orbitals are thus more centered on the ligands (that is on the π orbitals of difluorobenzene) than on the metal orbitals. This is apparent in the occupancy of d_{xz} and d_{yz} which is less than 1 shown in Table 1.

Discussions

First we study the π-electron level of 1,4-difluorobenzene, specifically, its splitting pattern from the parent benzene molecule subject to the perturbation by the two fluorine substituents. In Fig. 3, the splittings of the originally degenerate ($e_1(y)$, $e_1(x)$) pair and ($e_2(x^2-y^2)$, $e_2(xy)$) pair are 0.58 and 0.73 eV, respectively, due to antibonding combination of fluorine atom orbitals and benzene ring orbitals. Therefore one expects that due to a larger gap, the $[d_{x^2-y^2} \rightarrow e_2(x^2-y^2)]$ delocalization is less effective than the $d_{xy} \rightarrow e_2(xy)$ interaction. Furthermore, $[d_{x^2-y^2} \rightarrow e_2(x^2-y^2)]$ interaction is made worse by the orbital mixing between $e_2(x^2-y^2)$ and

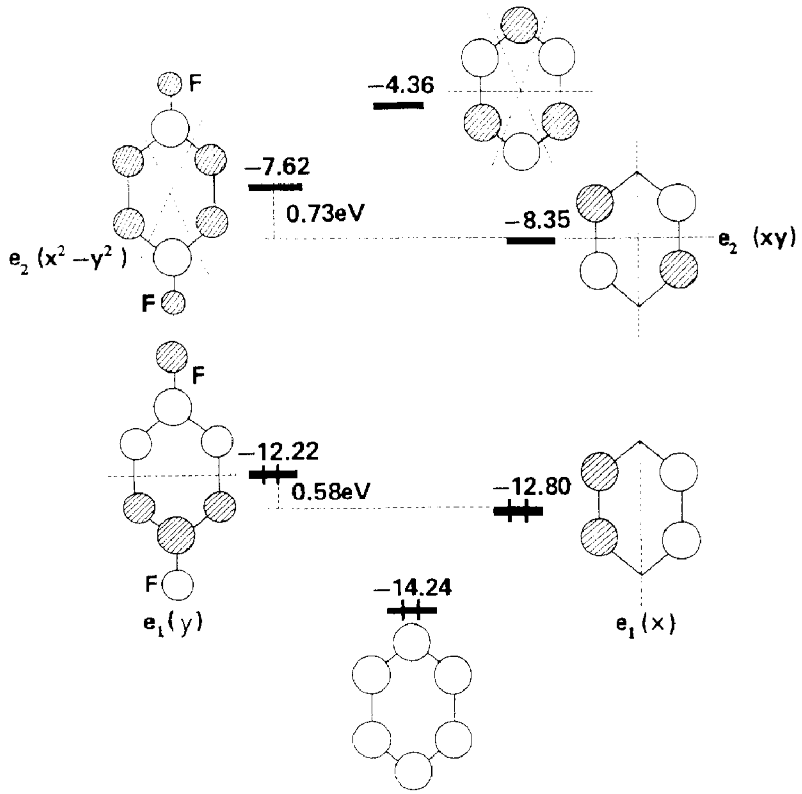

Fig. 3. The π electron energy level splitting pattern of 1,4-difluorobenzene.

a_g, the lowest π orbital of the ring in the D_{2h} geometry. The three orbital mixing [7] diagram depicted in Fig. 4 shows that there is a stabilization for $d_{x^2-y^2}$ of 0.3 eV. Figure 5 shows further that a similar effect exists not only for the 0° conformation, but for the 90° situation as well. For d_{xy} orbital, there is a good phase match between the metal d_{xy} and the vacant $e_2(xy)$ at either 0 or 90° with a better stabilization about 0.5 eV. These results explain an energy of gap about 0.2 eV between $d_{x^2-y^2}$ and d_{xy} at 0° and 90°. Figure 1 of also shows that the (d_{xy}, $d_{x^2-y^2}$) orbitals are degenerate at 45°. For this conformation, either d_{xy} or $d_{x^2-y^2}$ is able to interact with $e_2(xy)$ of one ring and $e_2(x^2-y^2)$ of the other. A similar situation exists for the d_{xz} and d_{yz} orbitals. The nondegeneracy of the d_{xz} and d_{yz} at 0° shown in Fig. 1 is an indirect result from the splitting between $e_1(y)$ and $e_1(x)$ due to an antibonding combination between ring orbital and fluorine orbitals in $e_1(y)$. At 90°, d_{xz} and d_{yz} are degenerate for either orbital consists of $e_1(y)$ from one ring and $e_1(x)$ from the other. It appears that the ($d_{x^2-y^2}$, d_{xy}) set favors a 45° comformation and the (d_{xz}, d_{yz}) set favors a 90° conformation for the two orbitals in each set can interact with an the upper or a lower ring orbital independently. The calculated conformation of 58° can be viewed as a compromise between the two angle (45°, 90°) for the dominance from the former set. The calculated rotational barrier is small, amounted to 0.02 eV. The barrier reflects a difference between two small quantities, namely, the delocalization interactions between metal e_2 set towards vacant e_2 set on the rings. The overlap between each metal orbital and the corresponding ring orbital is rather small.

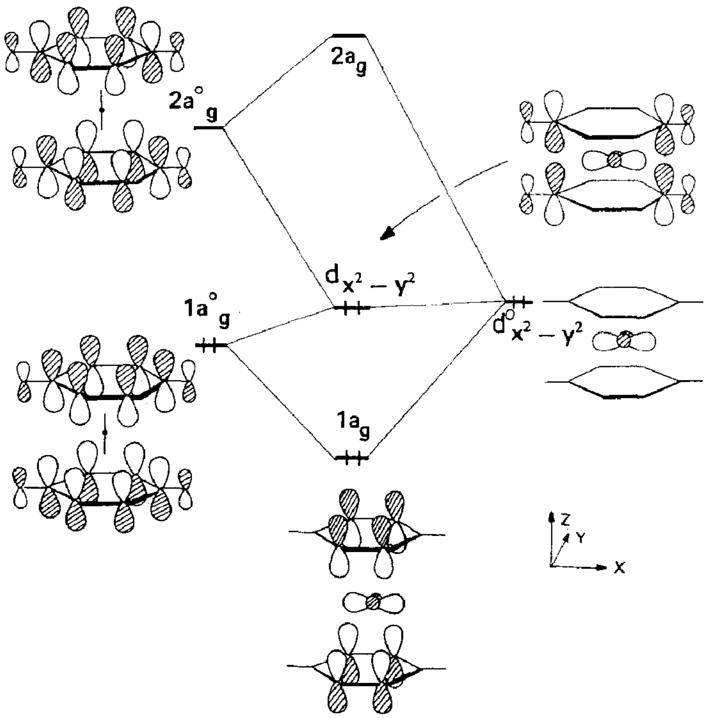

Fig. 4. The three-level-mixing among the metal $d_{x^2-y^2}$, the ring orbital $1a_g^0$ and $2a_g^0$ gives rise to the HOMO $d_{x^2-y^2}$ which has an antibonding character between the metal $d_{x^2-y^2}$ and atomic $2p_z$'s localized on C(1) and C(4).

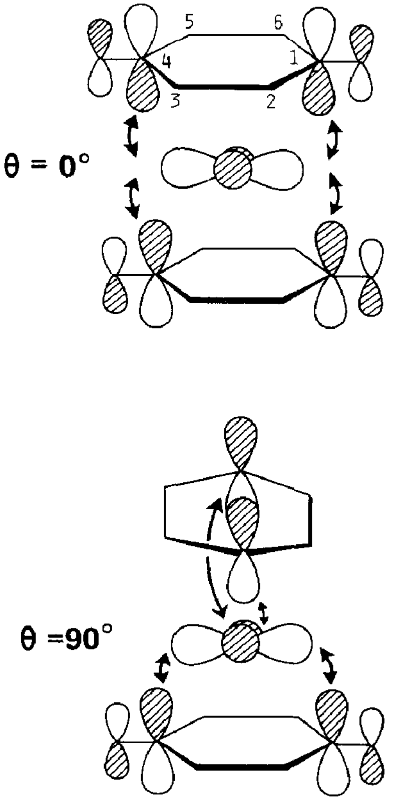

Fig. 5. The antibonding character of the HOMO $d_{x^2-y^2}$ is most important at the dihedral angle 0 ° and 90 °.

Table 2

Parameters used in the extended Hückel calculations [a] ionization potential (IP), Slater exponents (ζ), and coefficient (C) for double-ζ d functions

Orbitals	IP, eV	ζ_1	ζ_2	C(1)	C(2)
V 3d	−11.00	4.75	1.70	0.4755	0.7052
4s	−8.81	1.30			
4p	−5.52	0.875			
Cr 3d	−11.22	4.95	1.60	0.4876	0.7205
4s	−8.66	1.70			
4p	−5.24	1.70			
B 2s	−15.20	1.30			
2p	−8.20	1.30			
N 2s	−26.00	1.95			
2p	−13.40	1.95			
F 2s	−40.00	2.425			
2p	−18.1	2.425			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
H 1s	−13.60	1.30			

[a] See reference [5,6] for the parameters of V.

We expect the tiny barrier results from F being a weak π-donor. To make a comparison with this system, we consider some 1,4-disubstituted benzene rings with e_1 and e_2 split to a greater extent by some stronger π-donors or π-acceptors. First, the F atoms are replaced with planar NH_2 groups and planar BH_2 group, respectively. The rotation barriers are calculated to be 0.017 and 0.039 eV, with the corresponding dihedral angle 53 and 60°, respectively. Second, for stronger perturbations, the CH group of C(1) and C(4) of benzene ring are replaced with N atoms and BH^- groups, respectively. The rotation barriers for these heterocyclic complexes increase to 0.040 eV and 0.054 eV, with the corresponding dihedral angles 52° and 56°. These results appears to be coherent for their electronic effect. We have also calculated that in bis(*p*-xylene) vanadium, the dihedral angle shifts to 90° as expected for its apparent "steric effect". Its rotation barrier is 0.151 eV. Finally, we have calculated bis(1,4-difluorobenzene)chromium which has 18e with one more innocent d_{z^2} electron. The dihedral angle is 55° with a barrier of 0.035 eV, similar to the results for the vanadium system.

One interesting aspect of the HOMO-LUMO type interaction between the metal nonbonding orbital and the vacant ring orbital is that the population of the former drops while the orbital energy improves and vice versa as the dihedral angle changes. In Table 1, the metal 3*d* AO populations are shown. At (0°, 90°), the least stable conformations for $d_{x^2-y^2}$ orbital, its population shows a maximum. At 45°, the most stable one, the population shows a minimum. The results imply that metal $d_{x^2-y^2}$ to ring delocalization interaction is least effective at 0° and 90° and most effective at 45°. For comparison, the (d_{xz}, d_{yz}) pairs shows a similar variation, however, with a periodicity of 90° rather than 45° as for the ($d_{x^2-y^2}$, d_{xy}) pair.

Another interesting structural feature of the sandwich complex is a small boat deformation observed for the 1,4-difluorobenzene ligand [1,4]. The two fluorine substituted carbon atoms, C(1) and C(4), are displaced 0.06 Å from the plane of the ligand (see the top of Fig. 5 for the carbon labels). Therefore, the planes defined by atoms C(1), C(2) and C(6) and that by C(4), C(3) and C(5) are bent 5.4 and 5.7°, respectively, away from the metal. The average M–C(1) (C–F) distance is 2.204(3) Å as compared with 2.187(3) Å for the average M–C(2) (C–H). Our calculations with the planar ligand at a dihedral angle of 45° show that the bonding orbitals involving $(e_1(x), e_1(y))$ of the ligands and (d_{xz}, d_{yz}) of the metal have almost no contribution from C(1) and C(4). Therefore, the bonding lobe on the ligand is practically only localized in the central square region involving C(2), C(3), C(5) and C(6). Furthermore, as mentioned previously, the $d_{x^2-y^2}$ orbital has an antibonding interaction with the ligand $e_2(x^2-y^2)$ orbital. The latter is mainly localized on C(1) and C(4). The calculation and the observed results seem to agree with each other and with the notion that C(1) and C(4) are not as actively involved in the metal–ring bonding as the other four carbon atoms.

In conclusion, $d_{x^2-y^2}$ is the key orbital for the conformation of bis(1,4-difluorobenzene)vanadium system that accounts for both the dihedral angle between the two rings and the boat deformation for each ring. The detailed analysis shows that the $e_2(x^2-y^2)$ ring orbital is destabilized first by the orbital mixing with the fluorine atoms and secondly by the orbital mixing with the lowest ring orbital. The $d_{x^2-y^2}$ gains little from an out-of-phase mixing with $e_2(x^2-y^2)$ at the dihedral angle near 0° and 90°. However, at 45° $d_{x^2-y^2}$ is stabilized substantially when mixed with $e_2(xy)$ from the rotated ring so to result in the observed conformation near 45°.

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