vibrational spectrum has recently been questioned.22

The vibrational frequencies of $^3\text{B}_1$ and $^1\text{B}_1$ dimethylsilylene are listed in Table V. One interesting feature of these is the intensity pattern for the two modes occurring near 1400 cm$^{-1}$ which, by analogy with $^1\text{A}_1$, should be observed experimentally near 1200 cm$^{-1}$. In $^1\text{A}_1$, these were both observable with moderate to strong intensity; for $^3\text{B}_1$, they are predicted to both be very weak, and for $^1\text{B}_1$ only the lower mode has appreciable intensity. Another striking feature is that the out-of-plane CH$_2$ rocking modes $v_{10}$ and $v_{11}$ have been shifted up several hundred wavenumbers. Finally, we note that the symmetric and asymmetric Si–C stretches, $v_{33}$ and $v_{32}$, are now split by about 100 cm$^{-1}$ instead of being nearly degenerate. We hope these data will be of use to experimentalists.

Finally, to determine whether the species observed by Griller and co-workers could possibly be the triplet state of dimethylsilylene, we have determined CISD-Q energies of various triplet states at the $^3\text{B}_1$ optimized geometry with the DZ$^+\alpha$ basis set. Specifically, we have examined the $^3\text{A}_2$, $^3\text{A}_1$, and $^3\text{B}_1$ states which arise from the configurations $5\text{b}^28\text{a}^1$ ($^3\text{A}_2$), $5\text{b}^18\text{a}^1$ ($^3\text{A}_1$), and $5\text{b}^8\text{a}^0$ ($^3\text{B}_1$). These states are analogous to the lowest energy triplet states of SiH$_2$ found by Rice and Handy.12 The energy of $^3\text{A}_2$ is 127.5, 116.0, and 116.0 kcal/mol above $^3\text{B}_1$ at the SCF, CISD, and CISD-Q levels of theory, respectively. The corresponding values for $^3\text{A}_1$ are 128.5, 119.7, and 116.7 kcal/mol, and for $^3\text{B}_1$ we find 115.3, 113.3, and 112.3 kcal/mol. Thus we predict that excitations from $^1\text{B}_1$ to these higher lying triplets lie approximately 15–20 kcal/mol above the highest energy transitions observed by Griller (300 nm = 95.3 kcal/mol). While this suggests that the species observed by Griller is not $^3\text{B}_1$ dimethylsilylene, it is possible that larger basis sets and more highly correlated wave functions could reduce the splitting significantly.13 Of course, the minima on the excited triplet state surfaces will be below the vertical excitation energies given above. Our results, in this regard, are therefore inconclusive.

Conclusions

The first excited $^3\text{B}_1$ and $^1\text{B}_1$ states of dimethylsilylene are predicted to lie 25 and 54 kcal/mol above the ground state, respectively. We find a vertical excitation energy of 63 kcal/mol for the $^3\text{A}_1$–$^1\text{B}_1$ transition. This agrees very well with the spectroscopic observations of West, Michl, and co-workers who find the absorption maximum at 450 nm (62.7 kcal/mol). Thus we concur that the species observed by these researchers is due to ground-state dimethylsilylene and that the recent observations of Griller and co-workers to the earlier spectroscopic assignment are unfounded.

Acknowledgment. We thank Prof. J. Michl for sending us a preprint of their latest results prior to publication. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. The Berkeley theoretical chemistry minicomputer is supported by the U.S. National Science Foundation (Grant CHE-8218785).

Registy No. Si(CH$_3$)$_3$, 6376-86-9.

Donor–Acceptor Interaction and the Peculiar Structures of Dications

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Abstract: The geometries and stabilities of dications are explained by the donor-acceptor interaction of a (neutral) donor and an (doubly charged) acceptor molecule, respectively. The bonding in these donor-acceptor complexes is analyzed by means of one-electron density analysis. A simple model is presented to rationalize the bonding features of dications CH$_2$X$_2^{+}$ and CH$_4$X$_2^{+}$.

I. Introduction

In the last couple of years the experimental and theoretical study of doubly charged cations has become a very active field of chemical and physical research reflected in recent reviews on dications in solution and in the gas phase. Although doubly charged cations have been known since 1930, only in the last 10 years has this field become a topic of broad interest. This is largely due to the development of new experimental techniques in gas-phase ion chemistry such as charge-stripping mass spectrometry, PIPICO (photoion–photoion coincidence), and ISES (ion kinetic energy spectroscopy), to mention only a few in this rapidly developing field. In solution, the use of superacids and “magic acids” facilitates the investigation of dications.2 The interest in dications also arises from the finding that they exhibit some highly unusual structures. Doubly charged methane is planar,3 ethylene dication

Conclusions

The first excited $^3\text{B}_1$ and $^1\text{B}_1$ states of dimethylsilylene are predicted to lie 25 and 54 kcal/mol above the ground state, respectively. We find a vertical excitation energy of 63 kcal/mol for the $^3\text{A}_1$–$^1\text{B}_1$ transition. This agrees very well with the spectroscopic observations of West, Michl, and co-workers who find the absorption maximum at 450 nm (62.7 kcal/mol = 456 nm). Thus we concur that the species observed by these researchers is due to ground-state dimethylsilylene and that the recent observations of Griller and co-workers to the earlier spectroscopic assignment are unfounded.

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Registy No. Si(CH$_3$)$_3$, 6376-86-9.
Thus, dications exhibit a fascinating new field in chemistry. Dications, or higher charged species, may involve strongly bound helium and carbon atoms, and the electron transfer process is found to be much more efficient in dications than in monocations. In a review article, Bouma et al. discuss the principles which are presented here. The strength of the donor-acceptor interaction is determined by the geometry of the molecules involved and the electronegativity of the atoms. Theoretical calculations show that the donation of electrons from a donor molecule to an acceptor molecule results in a stabilization of the acceptor molecule. Therefore, donor-acceptor interaction has already been recognized as a stabilization for monocations in a class of structures called ion/dipole complexes or ylide structures. They can be described as ion/dipole complexes, where the electron donor is strongly bound to the electron acceptor by a hydrogen bond, and the negative charge center of a dipole is close to the positive charge center of a radical cation. Experimentally many ylide cations are well-known, among them CH$_2$F$^+$, CH$_2$OH$^+$, and CH$_2$NH$_2$$^+$+.

While these structures are not important for the neutral molecules, they often represent the global minimum on the potential energy surface of the radical cations. It will be seen that the structures of ylide cations can be explained by the donor-acceptor interaction of the contributing substituents, and they provided a model which predicts the existence and stability of hitherto unknown radical cations. Lammertsma has shown independently that a new class of dications, cation substituted methonium ions, can be explained in the same way as Koch and Frenking rationalized the ion/dipole complexes.

This paper reports a similar but greatly extended analysis of donor-acceptor interaction, which is found to be even more important in dications compared to the singly charged cations. While ylide monocations exist as isomers besides classical structures, and both of them are often found experimentally as isomeric species separated by a substantial barrier to rearrangement, dications with a classical structure are often not even a minimum on the potential energy surface but rearrange to the ylide dication. For example, charge-stripping experiments do not reveal any evidence for a methanol dication, but rather the methyleneoxonium dication CH$_2$OH$_2^+$ was detected in perfect agreement with theoretical predictions. It was shown that the unusual structures which were reported for many dications and overlooked in the case of CH$_2$H$_2^+$ and CH$_2$OH$_2^+$ could have easily been predicted with the principles which are presented here.

We present a simple model to rationalize the peculiar geometries, structures, and bonding features of dications CH$_2$X$^+$ and CH$_2$X$^+$ (X = F, OH, NH, N$_2$, F$_2$, H$_2$, CO, OC, CH$_3$ (A), CH$_4$). This model is based upon the idea that the stability, geometries, and electronic structures of the CH$_2$X$^+$ and CH$_2$X$^+$ dications can be explained by the interaction of a neutral donor molecule X and the electron acceptor CH$_2^+$ or CH$_4^+$ respectively. Thus, the CH$_2$X$^+$ and CH$_2$X$^+$ dications are considered as donor-acceptor complexes. In the course of our investigation of CH$_2$X$^+$ and CH$_2$X$^+$ structures we found that we can distinguish between three classes of compounds. The first comprises dications CH$_2$X$^+$, X = F, OH, NH, N$_2$, CO, OC, CH$_3$ (A), (type I complexes), where the electron acceptor CH$_2^+$ is bound to a closed-shell molecule X which donates electronic charge by a lone-pair orbital n.

The second class comprises dications CH$_2$Y$_2^+$ (type II complexes) with either Y$_2$ or H$_2$ donating electrons to CH$_2^+$ or CY$_2^+$ via a bonding o MO (o(H$_2$) or o(Y$_2$)) rather than a lone-pair orbital. In this work only two examples are discussed, namely Y$_2$ = H$_2$ and F$_2$.

Dications of the third class are formed by the interaction of two neutral donor molecules X and Y with the dication CH$_2$X$^+$.

Hence, type III complexes may be considered as a combination of type I and type II complexes. It will be seen that the structures of CH$_2$X$^+$ can best be understood when they are considered as the result of competition between X and Y to donate electrons to CH$_2^+$.

The strength of the donor-acceptor interaction is determined mainly by the frontier orbitals of the respective donor and acceptor molecules. Further insight into the electronic structure is achieved by using the one-electron density analysis. While most readers can be assumed to be familiar with the concepts of donor-acceptor interaction and frontier orbitals, this may not hold for the density analysis. The theoretical background of this technique has been described in detail somewhere else. Here we focus on the

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application of this method, and we will present in the next section only a short outline of the basic ideas in such a way that the nontheoretician can also use the information which is given here. Previous attempts to combine MO and electron density analysis have proven to be very successful,22-26 producing more reliable and comprehensive information of the electronic structure of molecules compared to familiar concepts such as the Mulliken population analysis.23

II. Quantum Chemical Methods

All MO calculations in this study have been performed with the CRAY version of GAUSSIAN 82.24 Geometry optimizations were carried out with a 6-31G* basis set. Additional single-point calculations include electron correlation incorporated at the third-order Möller–Plesset level of perturbation theory (frozen core).25 Hence, total energies have been obtained at the MP3/6-31G*/6-31G* level of theory.

The one-electron density distribution \( \rho(r) \) is analyzed with the aid of its gradient vector field \( \nabla \rho(r) \) and the Laplacian \( \nabla^2 \rho(r) \).26 Previous investigations have shown that \( \rho(r) \) exhibits local maxima only at the positions of the nuclei. Bonded atoms are linked by a path of maximum electron density, called bond path.27 The bond path can be considered as an image of the bond. A model has been developed to distinguish and to characterize covalent, ionic, hydrogen, and van der Waals bonds.24 The network of bond paths (bonds) linking a collection of atoms defines the molecular structure.25

Covalent bonds can be described by the properties of \( \rho(r) \) at the bond critical point \( r_0 \). The latter corresponds to the minimum of \( \rho \) along the bond path, and hence, to a saddle point of \( \rho \) in three dimensions. From the value of \( \rho_0 = \rho(r_0) \), a bond order \( n \) can be defined:

\[
\rho_0 = \nabla^2 \rho(r_0) + \frac{1}{2} \nabla^4 \rho(r_0) = \exp[A(n - 1)]
\]

with constants \( A \) and \( B \) depending on the nature of the atoms bonded together.22

Examination of the various quantities obtained in the one-electron analysis also showed that the matrix of second derivatives of \( \rho(r) \) (Hessian matrix) provides valuable information in regard to the electronic structure. The eigenvalues of the Hessian matrix yield the Laplacian of \( \rho(r) \). A negative (positive) value of \( \nabla^2 \rho(r) \) is indicative of local electron concentration (depletion) at \( r_0 \). The distribution \( \nabla^2 \rho(r) \) has been found to reflect the shell structure of atoms. In molecules, concentration lungs can be associated to electron bonds and electron lone pairs on the basis of simple models.26

In order to characterize the energetic aspects of a bond, the energy density \( H(r) \) has been defined24

\[
H(r) = H_0 - \frac{1}{2} n(r) \rho(r) = H_0 - \frac{1}{2} n \rho_0 \exp[A(n - 1)]
\]

\( n \) is known as bond order and \( n \), the bond critical point, is related to the minimum of \( \rho \) along the bond path. It is suggested that the existence of a bond path as a necessary and sufficient condition for the existence of a covalent bond.24

III. Results and Discussion

The calculated total energies of the neutral donor molecules X 1-9, the acceptor diatoms CH2+ 10 and CH2 11, and the donor-acceptor complexes CH3X2 28-37 are listed in Table 1. Structure 28 may formally be considered as belonging to both classes of donor-acceptor complexes, while CH2 11 represents formally the complex of CH2+ and H2. The optimized geometries are shown in Chart I. While some of the total energies have previously been reported, the only complete geometries of the donor-acceptor complexes 11,26 28-37.


(32) The constants \( A \) and \( B \) depend also on the basis set used. In the case of HF/6-31G* calculations \( A \) and \( B \) adopt the following values: 0.94, 1.52 \text{e}^2/\text{Å}^3 (CC); 0.78, 1.87 \text{e}^2/\text{Å}^3 (CN); 0.85, 1.77 \text{e}^2/\text{Å}^3 (CO).24

Figure 1. (a) Schematic representation of the \( \pi \) MOs of CH2+; (b) Contour line diagram of \( \nabla^2 \rho(r) \) calculated at the HF/6-31G* level of theory. Dashed lines indicate a value of \( \nabla^2 \rho(r) < 0 \) (charge concentration) and solid lines a value of \( \nabla^2 \rho(r) > 0 \) (charge depletion). The Laplacian of \( \rho \) is not shown for the inner-shell area of C. Heavy solid lines denote bond paths (paths of maximum electron density between atomic nuclei). The heavy dashed arrows point to the concentration hole in the valence sphere of the C atom.

Figure 2. Schematic presentation of the interaction of CH2+ with (a) \( n \)-donor X and (b) a \( \sigma \)-donor (\( \sigma \)-acceptor) X.22

22-26 and 36-39 are given in the literature. In order to discuss the results of donor-acceptor interaction, they are included in Chart I, together with the geometries of 11-11, taken from published data.33

(1) The Parent Dication CH2+ (10). Since we consider all dication 11-37 as donor-acceptor complexes of 10 and one or two neutral closed-shell molecules, it is advisable to discuss MOs and density features of CH2+ first. 10 possesses a linear geometry, which can be considered as the result of maximum overlap between sp-hybridized C orbitals and the 1s (H) orbitals. In addition,

Donor-Acceptor Interaction of Dications


Table I. Calculated Reaction Energies (kcal/mol) for Reactions 1, 2, and 3 at the MP3/6-31G*//6-31G* Level

<table>
<thead>
<tr>
<th>reaction</th>
<th>X</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂(¹A₁)</td>
<td>-273.3</td>
<td>-229.0</td>
<td>-45.6</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>-249.8</td>
<td>-203.5</td>
<td>-43.7</td>
<td></td>
</tr>
<tr>
<td>OH₂</td>
<td>-214.9</td>
<td>-151.4</td>
<td>-26.4</td>
<td></td>
</tr>
<tr>
<td>FH</td>
<td>-116.7</td>
<td>-89.4</td>
<td>-62.6</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-153.7</td>
<td>-135.3</td>
<td>-71.6</td>
<td></td>
</tr>
<tr>
<td>OC</td>
<td>-121.6</td>
<td>-79.9</td>
<td>-48.3</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>-126.9</td>
<td>-97.6</td>
<td>-60.7</td>
<td></td>
</tr>
<tr>
<td>F₂</td>
<td>-175.4</td>
<td>-117.2</td>
<td>+32.6</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>-90.0</td>
<td>-80.3</td>
<td>-80.3</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>-186.2</td>
<td>-134.0</td>
<td>-37.8</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Theoretically (MP3/6-31G*//6-31G*) and Experimentally Derived Proton Affinities (kcal/mol) of the Donor Molecules X

<table>
<thead>
<tr>
<th>X</th>
<th>calcd</th>
<th>explt</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂(¹A₀)</td>
<td>-221.9</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>-217.9</td>
<td>+20.9</td>
</tr>
<tr>
<td>OH₂</td>
<td>-198.4</td>
<td>+12.5</td>
</tr>
<tr>
<td>FH</td>
<td>-124.6</td>
<td>-126.0</td>
</tr>
<tr>
<td>CO</td>
<td>-145.4</td>
<td>-143, -139</td>
</tr>
<tr>
<td>OC</td>
<td>-107.6</td>
<td>+16.9</td>
</tr>
<tr>
<td>FH</td>
<td>-124.6</td>
<td>-126.0</td>
</tr>
<tr>
<td>N₂</td>
<td>-120.3</td>
<td>-116, -114</td>
</tr>
<tr>
<td>F₂</td>
<td>-89.2</td>
<td>-101.2</td>
</tr>
<tr>
<td>H₂</td>
<td>-125.1</td>
<td>-126, -128</td>
</tr>
</tbody>
</table>

Reference 40. Reference 41.

destabilizing electrostatic interactions between positively charged H atoms favor a linear geometry. Due to charge repulsion, the C-H bonds are longer in sp-hybridized CH₂⁺ compared to sp₂-hybridized CH₂ (¹A₁). There are two vacant degenerate pr orbitals at C (Figure 1a). This is reflected in the Laplace field of ρ(r) (Figure 1b) by holes of the charge concentration in the valence sphere of C, which form a torus surrounding the carbon atom perpendicular to the molecular axis.

(2) Type I Dications CH₂X₂⁺. If electronic charge is donated from a lone-pair orbital of a neutral molecule X to the vacant pr orbitals of 10, a donor—acceptor complex of type I is formed. Examples are structures 20-26. Rehybridization at the C atom from sp to sp² increases the orbital interactions between donor and acceptor (Figure 2a). The donor X may also possess filled pr orbitals, which can donate electrons to the second px(C) orbital of CH₂⁺. In addition, some donors X have empty or low-lying *MOs allowing back-donation from the pseudo-* C-H orbitals of CHP (hyperconjugation), thus increasing interactions between 10 and X (Figure 2b). The actual strength of the CX bond will depend on the α- and β-donor and *-acceptor ability of X. The strength of the donor—acceptor interaction in 20-26 can be determined by calculating the reaction energies ΔER of reaction 1 for type I dications:

CH₂X₂⁺ + H₂ → CH₂XH₂(²P)²⁺ + ΔER

The results shown in Table II establish the following order of donor strength for X in type I dications:

CH₂ > NH₃ > OH₂ > CO > N₂ > OC > FH

This may be compared with the theoretically and experimentally determined proton affinities listed in Table III which show the sequence

NH₃ > OH₂ > CO > N₂ > OC > FH (exptl)

CH₂ > NH₃ > OH₂ > CO > FH > N₂ > OC (calcd)

The comparison shows that (i) the stabilization sequence for the donor molecules X obtained for reaction 1 is very similar to what is found for the proton affinities of X; (ii) the computed values for ΔER of reaction 1 (117-273 kcal/mol) are always larger...
Chart I. Optimized Geometries (6-31G*) of Structures 1–37. Bond Lengths Are Given in Å and Angles in Deg

1. H-H 1.068 Å 109°

2. F-H 0.911 Å

3. H-H 1.055 Å 105.5°

4. H-H 1.050 Å 107°

5. F-F 1.345 Å 134.5°

6. N-N 1.099 Å

7. H-H 1.150 Å 114°

8. N-N 1.107 Å 110°

9. F-H 0.911 Å

10. H-H 1.045 Å 106°

11. H-H 1.044 Å 101°

12. H-H 1.041 Å 101°

13. H-H 1.038 Å 101°


15. H-H 1.037 Å 106°

16. H-H 1.035 Å 104°

17. H-H 1.035 Å 103°

18. H-H 1.035 Å 103°

19. H-H 1.033 Å 102°

20. H-H 1.031 Å 100°


22. H-H 1.027 Å 96°

23. H-H 1.025 Å 94°

24. H-H 1.023 Å 92°

25. H-H 1.021 Å 90°

26. H-H 1.019 Å 88°

27. H-H 1.017 Å 86°

28. H-H 1.016 Å 84°

29. H-H 1.014 Å 82°

30. H-H 1.013 Å 80°

31. H-H 1.012 Å 78°

32. H-H 1.011 Å 76°

33. H-H 1.010 Å 74°

34. H-H 1.009 Å 72°

35. H-H 1.008 Å 70°

36. H-H 1.007 Å 68°

37. H-H 1.006 Å 66°
but have the same order of magnitude as compared to the calculated proton affinities (80–229 kcal/mol) (Table III). The rather high $\Delta E_P$ values point to strong C–X bonding in these complexes. The donor strength of X in CH$_2$X$^+$ is plotted against the reaction energies $\Delta E_P$ of reaction 1. The correlation is obvious. Molecules X with a higher lying HOMO are better donors and show larger stabilization energies $\Delta E_P$ compared to species with a lower lying HOMO. This is exactly what frontier orbital theory predicts.

A comparison of the geometries of 20–26 with those of the separated donor and acceptor molecules (Chart I) reveals structural features which can be explained by the order of donor–acceptor interaction. Donation of electronic charge from X to CH$_2$$^+$ leads to binding of HCH and shortening of the C–H bonds in CH$_2$$^+$. Although steric interaction and hyperconjugation are additional factors determining the geometry, the magnitude of these changes follows quite closely the sequence of donor ability established above. At the same time, the bonds in the donor X become longer due to electron depletion. A notable exception is CO, which is discussed in detail below. While the interaction of the frontier orbitals accounts for most of the features found for the type 1 dications 20–26, the electron density analysis will show a more detailed picture of their electronic structure.

Relevant electron density properties determined at the bond critical point $r_b$ of the CX bond of type 1 complexes are summarized in Table IV. In agreement with the calculated stabi-
Table V. Comparison of Free and Complexed X in CH2X2+ on the Basis of $\rho(r)$ and $H(r)$.

<table>
<thead>
<tr>
<th>X</th>
<th>form</th>
<th>bond</th>
<th>$\rho_0$ (e/Å$^2$)</th>
<th>$\nabla^2\rho_0$ (e/Å$^4$)</th>
<th>$H_b$ (hartree/Å$^3$)</th>
<th>$\Delta\rho_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH</td>
<td>free</td>
<td>F–H</td>
<td>2.421</td>
<td>-68.979</td>
<td>-5.332</td>
<td>-67.9</td>
</tr>
<tr>
<td>OC</td>
<td>complex</td>
<td>O–C</td>
<td>1.003</td>
<td>-37.077</td>
<td>-2.698</td>
<td>-76.2</td>
</tr>
<tr>
<td>CO</td>
<td>free</td>
<td>O–C</td>
<td>3.372</td>
<td>41.543</td>
<td>-5.527</td>
<td>-34.0</td>
</tr>
<tr>
<td>CO</td>
<td>complex</td>
<td>O–C</td>
<td>2.478</td>
<td>24.705</td>
<td>-3.558</td>
<td>-35.4</td>
</tr>
<tr>
<td>NN</td>
<td>free</td>
<td>N–N</td>
<td>4.801</td>
<td>-66.499</td>
<td>-8.776</td>
<td>0</td>
</tr>
<tr>
<td>OH2</td>
<td>complex</td>
<td>O–H</td>
<td>3.372</td>
<td>41.543</td>
<td>-5.527</td>
<td>34.0</td>
</tr>
<tr>
<td>NH3</td>
<td>free</td>
<td>N–H</td>
<td>2.312</td>
<td>-41.739</td>
<td>-3.272</td>
<td>-49.3</td>
</tr>
<tr>
<td>CH2  ($^1A_1$)</td>
<td>free</td>
<td>C–H</td>
<td>1.908</td>
<td>-25.285</td>
<td>-1.980</td>
<td>-28.3</td>
</tr>
</tbody>
</table>

* $\Delta\rho_0$ denotes the deviation of the bond critical point $\mathbf{r}_b$ from the midpoint of the bond considered. A negative (positive) $\Delta\rho_0$ corresponds to a shift of $\mathbf{r}_b$ toward the second (first) atom of the bond. * Averaged values.

The $\nabla^2\rho(r)$ diagram displays the charge concentration between C and N but also the holes in the charge concentration in the valence sphere of carbon above and below the molecular plane. These holes are found for all type I dications. They reveal that CH2X2+ is capable of interacting with another donor.

(3) Type II Dications CH2Y2+.

From a structural point of view, type II dications are more interesting than type I dications. Type II dications are formed if electron density is transferred from bonding $\sigma$-MOs rather than lone-pair orbitals of the donor molecules to CH2X2+ (CY2)2+ (Figure 5a). Structures II and 27 are examples investigated here. In addition, there can be back-donation from the pseudo-$\pi$ orbital of the CH2X2+ (CY2)2+ group to $\sigma^*(Y_2)$ ($\sigma^*(H_2)$) (Figure 5a). Depending on the strength of the two types of interactions, the structural situations shown in Figure 6 can develop: (a) The $\sigma(Y_2)$ MO is low in energy. Only a small amount of charge is donated. There is no back-donation. A loose complex with a T-structure (Figure 6, a) is formed. (b) $\pi$-back-donation from CH2 is stronger than $\sigma$-donation leading to bond paths between Y and C. A three-membered ring structure is formed (Figure 6, b). (c) $\sigma$-donation from the $\pi(Y_2)$ MO is fully developed, as is $\pi$-back-donation into the $\sigma^*(Y_2)$ MO. An open structure develops, and the Y–Y $\sigma$-bond is broken (Figure 6, c). The latter situation applies to CH2+ 11 where Y2 and H2 are identical which leads to a square-planar structure. (d) In the way $\sigma$-donation and $\pi$-back-donation between CH2X2+ and Y2 increase, the CY bonds become stronger at the expense of the CH bonds. Thus, CH2Y2+2 eventually changes to a donor–acceptor complex between CY2 and H2, again with the possibility of adopting a ring or a T-structure (Figures 6, d and e).

In the case of Y2 = F2 (27), there is competition between electron donation from H2 and F2. The H–H bond is much stronger compared to the F–F bond, making F2 a better $\pi$-donor. In addition, the F atoms can donate $\pi$-electron to the empty $\pi^*(C)$ orbital (Figure 5b) thus enhancing the strength of the CF bonds. At the same time, the CH bonds are weakened by electron donation from the $\pi$ (n12–n2) in-plane combination of lone-pair orbitals into the CH2 pseudo-$\pi^*$ MO (Figure 5b). However, the molecule can stabilize by changing from a planar to a perpendicular arrangement of the CF2 and H2 entities (Figure 5c). Although there are again two kinds of orbital interaction, one which strengthens the CF bonds and one which weakens the CH bonds, the overall effect is now more stabilizing since orbital overlap has been increased for the first kind of interaction and decreased for the second one (Figure 5c). As a result CF2H2+ 27 adopts the three-membered ring structure (Figure 6, d) as is.
verified by the data given in Table VI and the \( \nabla \rho \) plot for 27 depicted in Figure 7. The latter reveals that electron density is totally delocalized in the HHC plane between the three nuclei, which are connected by bond paths (solid lines in Figure 7).

The discussion presented above indicates that the electronic structure of \( \text{CH}_2\text{F}_2^{2+} \) cannot simply be considered as frontier orbital interaction between \( \text{CH}_2^{2+} \) and \( \text{F}_2 \). Thus, the calculated stabilization energy for \( X = \text{F}_2 \) in reaction 1 (\(-175.4 \text{ kcal/mol, Table II}\)) is much larger as it might have been predicted from the computed proton affinity of \( \text{F}_2 \) (89.2 kcal/mol, Table V). For \( X = \text{H}_2 \), however, the calculated values for \( \Delta E_{\text{R}} \) of (1) and proton affinity agree with the sequence of donor ability predicted for various donors \( X \) (Tables II and III).

The optimized structure 27 for \( \text{CH}_2\text{F}_2^{2+} \) corresponds to donor–acceptor interaction between \( \text{CF}_2^{2+} \) and \( \text{H}_2 \), rather than \( \text{CH}_2^{2+} \) and \( \text{F}_2 \). We calculated the energy of hydrogenation of \( \text{CF}_2^{2+} \) leading to \( \text{CH}_2\text{F}_2^{2+} \). At the MP3/6-31G*//6-31G* level, the reaction energy is \(-59.4 \text{ kcal/mol,} \) which is much less compared to the hydrogenation reaction of \( \text{CH}_2^{2+} \) (\(-90.0 \text{ kcal/mol, Table II}\)).

The eigenvalue \( \lambda_{\text{LUMO}} \) of \( \text{CF}_2^{2+} \) is substantially lower (-16.07 eV, 6-31G*//6-31G*), compared with \( \text{CH}_2^{2+} \) (-19.25 eV, 6-31G*//6-31G*). Thus, the lower hydrogenation energy of \( \text{CF}_2^{2+} \) is explained by frontier orbital interaction.

(4) Type III Dications \( \text{CH}_2\text{X}(\text{Y}^2)^{2+} \). Due to the fact that there are still large charge-concentration holes in the valence sphere of carbon (corresponding to vacant \( \pi \) orbitals) in \( \text{CH}_2\text{X}^{2+} \) dications (Figure 8), a second donor either of type \( X \) (with a lone-pair orbital) or type \( Y \) can be coordinated at \( C \). In this work we consider only the latter case with \( Y = \text{H} \), i.e., structures 28–36, which may therefore be considered as hydrogenated forms of 20–27.

37 is a special case which arises from doubly hydrogenated 20 (or singly hydrogenated 28). This has already been recognized by Lammertsma et al.12b

In Figure 8 orbital interactions between the two donor molecules \( X \) and \( H_2 \) and the acceptor \( \text{CH}_2^{2+} \) are shown. Donation from an \( n \)-orbital will be stronger than that from the \( \sigma(\text{H}_2) \) MO (Figure 8a). Besides donation from the \( \sigma \)-type lone-pair orbital, some of the donors \( X \) can donate electronic charge from filled \( n \)-orbitals into the empty \( \pi^*(\text{C}) \) orbital (Figure 8a) and pseudo-\( \pi \)-MO of \( \text{CH}_2^{2+} \) (Figure 8b). However, there is now competition for electron donation into the empty \( \pi^*(\text{C}) \) orbital between \( \sigma(\text{H}_2) \) and \( \pi(\text{X}) \) orbitals (Figure 8). Furthermore, back-donation of the partially filled \( \pi^*(\text{C}) \) orbital into the \( \pi^* \) MO is possible for some donors \( X \) (Figure 8c). Hence, \( H_2 \) donation will depend on the extend and type of \( X \) donation, as will the extent of back-donation from the pseudo-\( \pi \)-MO of \( \text{CH}_2^{2+} \) to \( \pi^*(\text{H}_2) \) (Figure 8b). As in the case of \( \text{CH}_2\text{X}(\text{Y}^2)^{2+} \) dications (Figure 6), one can expect open, ring, and T structures for \( \text{CH}_2\text{X}(\text{H}^2)^{2+} \) dications. The actual structure and the specific geometry of type III dications will depend on the relative donor ability of \( X \).

Table VII. Structure of the \( \text{C}(\text{H})_2^+ \) Unit of \( \text{CH}_2\text{X}(\text{H}^2)^{2+} \) Dications in Dependence on the Structure of \( X \)

<table>
<thead>
<tr>
<th>( X )</th>
<th>( R(\text{H–H}) ) (( \text{Å} ))</th>
<th>( \mu_0(\text{C–H}) ) (e/( \text{Å}^3 ))</th>
<th>structure characterization of ( X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.492</td>
<td>1.478</td>
<td>open ( \sigma/\pi )-donor, ( \sigma )-acceptor</td>
</tr>
<tr>
<td>NN</td>
<td>0.981</td>
<td>1.364</td>
<td>open ( \sigma/\pi )-donor, ( \sigma )-acceptor</td>
</tr>
<tr>
<td>FF</td>
<td>0.933</td>
<td>1.347</td>
<td>open weak ( \sigma )-donor, ( \sigma )-donor</td>
</tr>
<tr>
<td>FH</td>
<td>0.917</td>
<td>1.355</td>
<td>open weak ( \sigma )-donor, ( \sigma )-donor</td>
</tr>
<tr>
<td>OC</td>
<td>0.911</td>
<td>1.352</td>
<td>open weak ( \sigma )-donor, ( \sigma )-donor</td>
</tr>
<tr>
<td>CH(_2) (( \text{A}_1 ))</td>
<td>0.901</td>
<td>1.333</td>
<td>open ( \sigma )-donor</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>0.894</td>
<td>1.337</td>
<td>open ( \sigma )-donor</td>
</tr>
<tr>
<td>OH(_2)</td>
<td>0.866</td>
<td>1.294</td>
<td>ring ( \sigma )-donor, ( \sigma )-donor</td>
</tr>
</tbody>
</table>

Table VIII. Comparison of the Bond Orders \( n \) of the \( CX \) Bond in \( \text{CH}_2\text{X}(\text{Y}^2)^{2+} \) (Type I) and \( \text{CH}_2\text{X}(\text{H}^2)^{2+} \) (Type III) Dications

<table>
<thead>
<tr>
<th>( X )</th>
<th>( I )</th>
<th>( III )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH(_2)</td>
<td>(&lt;1)</td>
<td>(&lt;1)</td>
</tr>
<tr>
<td>OC</td>
<td>0.97</td>
<td>0.72</td>
</tr>
<tr>
<td>NN</td>
<td>0.94</td>
<td>0.75</td>
</tr>
<tr>
<td>OH(_2)</td>
<td>1.19</td>
<td>0.89</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>1.20</td>
<td>0.94</td>
</tr>
<tr>
<td>CO</td>
<td>1.25</td>
<td>1.22</td>
</tr>
<tr>
<td>CH(_2) (( \text{A}_1 ))</td>
<td>1.84</td>
<td>1.46</td>
</tr>
</tbody>
</table>

\( \rho_0 = 1.423 \) (I) and 1.080 e/\( \text{Å}^3 \) (III).

In the following we discuss the influence of \( X \) on the interactions of \( \text{CH}_2^{2+} \) and \( \text{H}_2 \). It is easy to see that these interactions depend strongly (i) on the electron population of the \( \pi(\text{C}) \) orbital in \( \text{CH}_2\text{X}^{2+} \) and (ii) on the total charge at \( C \) and the resultant effective electronegativity of \( X \). Both (i) and (ii) in turn depend on the \( \sigma/\pi \)-donor ability of \( X \).

In Table VII relevant information on the structure of type III dications in dependence on the nature of \( X \) is summarized. If \( X \) is both a \( \sigma/\pi \)-donor and a \( \pi \)-acceptor (because of a low-lying \( \pi^* \) MO) as in the case of \( X = \text{CO} \) and \( \text{N}_2 \), then the \( \pi \)-acceptor ability of \( X \) causes electron withdrawal from \( \text{H}_2 \) (Figure 8b). \( \pi \)-donation from a filled \( \pi(X) \) MO into the pseudo-\( \pi \)-MO (Figure 8b) leads to (i) weakening of the \( C-H \) bonds of the \( \text{CH}_2^{2+} \) acceptor and (ii) strengthening of the \( \text{H}_2-C-Y \) bonds (Figure 8b). In the case of \( X = \text{CO} \), all four \( C-H \) bonds are now equal (Table VII).

If \( X = \text{OH}_2 \), then the \( \sigma \) and \( \pi \)-donor ability of \( X \) will largely prevent \( \pi \)-withdrawal from \( \text{H}_2 \). However, at the same time \( C-H \) geometry.
interactions are established via the pseudo-σ MO (Figure 8b). As a consequence, a three-membered ring structure is found (compare with Figure 7). The H-H and C-H bond paths are strongly curved inward, indicating that all ring bonds are weak. RELATIVELY SMALL ELECTRONIC CHANGES WILL LEAD TO EITHER THE OPEN OR THE T STRUCTURE OF THE DONOR-ACCEPTOR COMPLEX.

A comparison of the C-X bond properties of type III dications with those found for type I dications (Table VIII) is helpful when assessing the actual donor ability of X in the presence of H2 as the second donor. In all cases considered the bond order r is decreased in type III complexes, indicative of a reduced donor activity of X. The decrease in the bond order is smallest for CO and largest for OH2.

The stabilization due to electron donation from X in type III dications can be determined by calculating the reaction energies \( \Delta E_R \) for reaction 2.

\[
\text{CH}_2X^+ + X \rightarrow \text{CH}_2X(X)^+ + \Delta E_R
\]

(2)

The calculated results shown in Table II support the conclusion that the donor selectivity of X is reduced in type III complexes compared to type I dications. In all cases the \( \Delta E_R \) values are smaller for reaction 2 than for reaction 1. However, the relative donor ability is nearly the same and comparable to the order of proton affinities. The following sequence is found for reaction 2:

\[
\text{CH}_2 > \text{NH}_3 > \text{OH}_2 > \text{CO} \sim \text{CH}_2 > \text{N}_2 > \text{FH} > \text{H}_2 \sim \text{OC} > \text{F}_2
\]

Contrary to type I dications, a lone pair donor structure with X = F2 could be located (35) for CH2X3+. The computed relatively small \( \Delta E_R \) value for 35 in reaction 2 is in agreement with the calculated low proton affinity of F2. The correlation of the eigenvalues of \( \sigma_{\text{HOMO}} \) of X with \( \Delta E_R \) of reaction 2 is shown in Figure 3. The donor-acceptor interaction is clearly a function of the frontier orbital energy levels. The lower lying LUMO of CH2X3+ (tLUMO = -19.25 eV) also explains the larger interaction in Type I dications compared to CH2X1+ structures (tLUMO(19CH3) = -16.48 eV).

The optimized geometries of 28-36 are in agreement with the argumentation presented here. All C-X bonds are longer compared to the respective type I dication. The bond lengthening in X resulting from donor-acceptor interaction is less pronounced, and besides CO N2 also has a shorter bond compared to the isolated molecule. Due to distortion from local \( \sigma_{\text{C}} \) symmetry of the CH4 unit, CHAB2+ structures deviate more or less from linearity in C-A-B (with the exception, of course, of AB = CO), and X = OH2 is found with a nonplanar arrangement.

The geometries and stabilities of dications can in many cases be rationalized by the donor and acceptor strength of constituting subunits. In this way the existence of unusual structures such as CHX5+ 20-27 and CHX4+ 28-37, which are unknown or very unstable as neutral molecules, finds a logical explanation. The detailed examination of the geometries and bonding features of the dications investigated here leads to three different classes of dications which are distinguished by the type and number of donor-acceptor interaction. The simple donor-acceptor model presented here may be used to predict unknown dications or to explain results of experiments or quantum chemical calculations. To illustrate this, two examples taken from the literature shall shortly be discussed.

In a combined experimental and theoretical investigation, Koch et al. reported that the global minimum of CH2O2+ corresponds to the oxoniomethylene dication HC-OH22+ (A). It was found to be 22.7 kcal/mol lower in energy than the second minimum, the hydroxymethyl dication H2C-OH2+ (B). A third structure, the methoxy dication H2C-O-2+ (C), is 116.8 kcal/mol higher in energy than A. Could this result be predicted with use of the donor-acceptor model for CHX5+? The answer is yes. A, B, and C can be considered as donor-acceptor complexes arising from acceptors CH2+, CH22+, and CH32+ and donors OH2, OH, and O. The frontier orbitals establish a sequence of donor strength OH2 > OH > O, and the acceptor strength is found as CH22+ > CH2+ > CH3+29. Thus, the stability order is in perfect

\[ \text{CH}_2X2+ \text{with a second donor Y:} \]

The following sequence is found (Table VII):

\[
\text{CO} > \text{N}_2 > \text{FH} > \text{OC} > \text{CH}_2 > \text{NH}_3 > \text{OH}_2
\]

Both sequences are nearly identical and demonstrate that the stabilization which can be expected from interaction of type I

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Both sequences are nearly identical and demonstrate that the stabilization which can be expected from interaction of type I
Barriers to Rotation Adjacent to Double Bonds. 2. n-Propyl vs. Isopropyl Groups

Kenneth B. Wiberg

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. Received March 28, 1986

Abstract: The barriers to rotation about the C–C bonds adjacent to the carbonyl groups of isobutyaldehyde, methyl isopropyl ketone, and isobutyric acid were calculated. The 3-21G basis set was used for the geometry optimizations, and the 6-31G* basis set was used to obtain the energies. The differences in energy between R = n-propyl and isopropyl also were calculated and reproduced the observed energy differences. Whereas the more branched isomer had a significantly lower energy for the aldehydes and acids, the difference in energy was very small with the ketones. The components of the barrier are discussed. The traditional decomposition into 1-, 2-, and 3-fold terms does not provide a useful representation of the interactions which are involved. Besides the 3-fold barrier observed with compounds having R = CH₃, the major contributions to the barrier arise from the stabilizing interaction between an allyl group and the carbonyl (~1 kcal/mol) and from the repulsive interaction between one of the methyls of the isopropyl group and the other substituent at the carbonyl. A hydroxy group (i.e., in isobutyric acid) leads to a significantly smaller steric interaction than found with a methyl group (i.e., in a methyl alkyl ketone).

The conformations of ketones have been of considerable interest in connection with studies of stereoselection in addition to the carbonyl group. Models for the addition have been developed by Cram, Cornforth, Karabatsos, Felkin, and others. Theoretical studies of the activated complexes for addition to carbonyl groups by Ruch and Ugi, Salem, and especially Anh and Eisenstein


It seems that no suitable donor unit for C₆H₅ can be formed which can interact in a favorable way with CH₃⁺. In this context it is interesting to learn that in the meantime the same 13 structures have been calculated for the triply charged C₆H₅⁺ isomers. Again, structures A, B, and C were found as energetically lowest lying species, but the stability differences were found to be larger at the same level of theory. It seems that the differences in donor–acceptor interaction become more pronounced in higher charged species.

Our analysis of donor–acceptor interaction does not cover all kinds of possible orbital interaction. For example, stable structures may arise from donor–acceptor interaction involving π-donors. Hexacoordinated pyramidal carbocations, a well-known class of cations which is even stable in solution, can be explained by the interaction between an apical RC⁺ acceptor and a basal π-donor. Thus, the model of donor–acceptor interaction may still be extended.

It is more the rule than the exception that the structure of a doubly charged species is substantially different compared to the respective neutral molecule. The simple model presented here is of great value for predicting structures of stable dications.

Acknowledgment. This work has financially been supported by the Fonds der Chemischen Industrie. G.F. thanks Dr. Jack Collins for stimulating discussions and constructive criticism on a preliminary version of the manuscript. D.C. thanks the Deutsche Forschungsgemeinschaft and the Rechenzentrum der Universität Köln for support. W.K. thanks Nikolaus Heinrich for helpful discussions.

(46) A different analysis has been given by the following: Jennis, E. D.; Schleyer, P. v. R. J. Am. Chem. Soc. 1982, 104, 4781.

(42) For a discussion and further examples of planar, substituted ethylene dications see ref 35.
(43) This is a qualitative approach to demonstrate the basic principle. A more detailed account of frontier orbital interaction has to consider orbital coefficients. For example, the different reaction energies when CO donates electronic charge via oxygen or carbon may be explained by the larger coefficient at carbon for the lone-pair HOMO. For further discussion of frontier orbital interaction, see ref 21.
(44) The total energy of CR₂⁺ at MP3/6-31G*/6-31G* is -235.9412 hartrees. The geometry was taken from the following: Koch, W.; Frenking, G. Chem. Phys. Lett. 1985, 114, 178.

3. n-Propyl and Isopropyl also were calculated in n-propyl and isopropyl. The 3-21G basis set was used for the geometry optimizations, and the 6-31G* basis set was used to obtain the energies. The differences in energy between R = n-propyl and isopropyl also were calculated and reproduced the observed energy differences. Whereas the more branched isomer had a significantly lower energy for the aldehydes and acids, the difference in energy was very small with the ketones. The components of the barrier are discussed. The traditional decomposition into 1-, 2-, and 3-fold terms does not provide a useful representation of the interactions which are involved. Besides the 3-fold barrier observed with compounds having R = CH₃, the major contributions to the barrier arise from the stabilizing interaction between an allyl group and the carbonyl (~1 kcal/mol) and from the repulsive interaction between one of the methyls of the isopropyl group and the other substituent at the carbonyl. A hydroxy group (i.e., in isobutyric acid) leads to a significantly smaller steric interaction than found with a methyl group (i.e., in a methyl alkyl ketone).