hydrogens in a given molecule shows that the binding of the charge transferred to the A atom is significantly increased and is one of the principal contributors to the attractive energy contributions to the barriers in these molecules.

The phosphorus atom is slightly destabilized in the planar geometry in spite of being the recipient of a transfer of charge from the hydrogen atoms. While small changes in the charge distribution of an atom lead to small changes in its energy, it is possible that a change in the distribution can be such as to result in a near-cancellation of the changes in the attractive and repulsive contributions, as occurs for the phosphorus atom in the inversion of PH_3. This differing behavior of a second- and third-row atom can be accounted for in terms of the larger size of the latter atom. The magnitude of the decrease in the value of $V_a°$ for the second-row atoms is greater than half the total decrease in $V_a(\Omega)$ (Table III). The charge transferred to the P atom, however, is relatively less effective at stabilizing the atom, since the added density is further from the attractive force of the nucleus. There is a smaller increase in stability per added electron for P than for N or O. The diffuse nature of the phosphorus charge distribution is reflected in the very large increase in its quadrupole polarization that accompanies the transfer of charge to this atom in the attainment of the planar structure, $Q_{zz}(P)$ changing from −4.2 to −13.1 au. The decrease in the A–H bond length in attaining the planar geometry is largest in PH_3, and this atom has the largest relative increase in its repulsive energy contributions. Both the A and H atoms are destabilized in PH_3, and the inversion barrier in this molecule is six times larger than the barrier in NH_3.

Conclusions

The observations made here regarding the changes in energy and geometry associated with internal rotations and inversions should be of general applicability. For example, the same observations apply to the origin of the barrier to internal rotation about the C–O bond in carboxylic acids and esters, as studied by Wiberg and Laidig.[24] Their calculations predict formic acid, methyl formate, acetic acid, and methyl acetate to possess a minimum energy planar Z conformation. Like the rotational barriers studied here, they find the principal geometry change associated with the attainment of the nonplanar conformation to be a lengthening of the bond about which the rotation occurs, and the barriers to arise from an increase in the attractive potential energy and in spite of a decrease in the repulsive interactions. The largest energy changes occur for the C and O atoms of the rotated bond, the carbon being stabilized and the oxygen being destabilized in the nonplanar rotamer.

The origin of the barrier for the rotation of planar formamide by 90° or 270° was also investigated.[24] This is an interesting case, as here the rotation about the C–N bond results in the pyramidalization of the N atom and its formal hybridization changes from sp^2 to sp^3. Thus, as for the inversion barriers discussed above, the N atom is found to gain electronic charge from its bonded neighbors and to increase in stability when the amide group is rotated from a nonplanar into its planar form. In this molecule, however, the destabilization of the atoms that donate charge to the N atom in the planar geometry is less than the stabilization achieved by the N atom, and the equilibrium geometry of this molecule is planar. Here again, the principal geometrical change is a lengthening of the bond about which rotation occurs (as in the inversion of ammonia, the bonds to N are shortest when its s character is greatest), and the predicted barrier of 16.0 kcal/mol is a result of an increase in the attractive potential energy and a decrease in the repulsive energies. Because of the transfer of charge from N to C that accompanies the loss of planarity, most of the lengthening of the C–N bond, which equals 0.15 au, is taken up by an increase in the bonded radius of the carbon atom, from 0.83 to 1.04 au. The resonance model accounts for the relative stability of the planar geometry by invoking a resonance structure wherein the N atom donates charge to the carbonyl oxygen atom, a resonance interaction that is lost upon rotation. The resonance model is, therefore, in direct contradiction with the hybridization model for these systems, which predicts the N to be most electronegative in the planar structure. The theory of atoms in molecules shows the resonance model to be wrong in this instance.[24] Not only is the direction of the charge transfer for N incorrect, the properties of the oxygen atom, including its geometrical parameters, are found to change by only small amounts compared to the changes undergone by the C and N atoms, the magnitude of its energy change being 20–30 times smaller. This conclusion is not some artifact of the theory of atoms in molecules. It is a result of the observation that the distribution of charge over the basin of the oxygen atom—a well-defined region of real space extending to within 0.74 au of the carbon nucleus—is only slightly perturbed by a rotation about the C–N axis. Siggel et al.[25] make the same criticism of the resonance model with regard to its explanation of the relative acidities of carboxylic acids and alcohols. The enhanced acidity of the former over the latter is accounted for by the inductive effect, as measured by spatially determined atomic populations, rather than increased resonance stabilization of the carboxylate anion.

An atomic property and its change are determined by the distribution of electronic charge and its change over the basin of the atom and are model-independent. Because of this, the theory may be used to test existing models and aid in the construction of new ones.

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Two Isomers of the $Li_2C_2O_2$ Molecule: An ab Initio Study

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Abstract: Ab initio calculations at the HF/6-311G* and MP2/6-311G* levels reveal the existence of two isomers of the $Li_2C_2O_2$ molecule. The linear structure corresponds to the dilithium salt of dihydroxyacetylene. The second stable structure possesses two four-membered rings, each consisting of one lithium, one oxygen, and two carbon atoms. At both the HF and MP2 levels, the two isomers are predicted to have very close energies. The GAPT atomic charges and vibrational frequencies are calculated for both structures, and the bonding is analyzed with the aid of Bader's topological theory of atoms in molecules. The results of the theoretical calculations rationalize the recent experimental observations.

Introduction

Contrary to popular belief, urea was not the first organic compound ever synthesized from inorganic substrates and benzene was not the first aromatic compound ever isolated. In 1825, Gmelin isolated yellow dipotassium salt of crocoic acid from the material obtained by heating potassium hydroxide and carbon.[1]

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Table I. Results of the HF/6-311G* and MP2/6-311G* Calculations on the Two Isomers of the $Li_2C_2O_2$ Molecule

structure	linear	cyclic
E_{HF}, au	−240.396 571 5	−240.396 194 4
E_{MP2},[a] au	−241.165 954 6	−241.158 254 4
ΔE_{HF},[b] kcal/mol	0.0 (0.0)	0.2 (−0.8)
ΔE_{MP2},[a,b] kcal/mol	0.0 (0.0)	4.8 (3.8)
GAPT atomic charges at the HF level		
Q_{Li}	0.9211	0.7092
Q_O	−1.2819	−0.8075
Q_C	0.3608	0.0983
vibrational freq at the HF level, cm^{-1} (IR intens)	100 (2 × 197)	147 (77)
	133 (0)	234 (62)
	378 (2 × 19)	407 (112)
	539 (0)	430 (0)
	639 (0)	444 (0)
	877 (299)	491 (180)
	1179 (0)	517 (0)
	1504 (1277)	608 (135)
	2595 (1097)	640 (0)
		1019 (0)
		1700 (0)
		1742 (455)

[a] At the HF geometries. [b] Zero-point energy corrected (HF vibrational frequencies, no scaling), values in parentheses.

This predated both Wöhler's classical synthesis of urea and Faraday's isolation of benzene from coal tar. Nine years later, it was realized that potassium metal reacts with carbon monoxide to form the hexapotassium salt of hexahydroxybenzene, $K_6C_6O_6$,[2] which is readily oxidized to potassium rodizonate and potassium croconate. Only more than a century later, the mechanism of formation of $K_6C_6O_6$ was clarified.[3]

The gray $K_6C_6O_6$ is now believed[4] to be a product of trimerization of the black $K_2C_2O_2$, which is formed from potassium metal and carbon monoxide when the reaction is carried out at low temperature. Weiss and Büchner[5] inferred from their X-ray studies that $K_2C_2O_2$ is the dipotassium salt of dihydroxyacetylene. The same linear structure was assigned to the yellow product obtained by reacting potassium and carbon monoxide in liquid ammonia. Subsequently, the structures of $Na_2C_2O_2$,[6] $Rb_2C_2O_2$, and $Cs_2C_2O_2$[7] were investigated, and all these compounds were found to be analogous to $K_2C_2O_2$. However, the $Li_2C_2O_2$ species eluded experimental studies due to its extreme instability (it explodes at room temperature).[8]

Recently, Krishnan et al.[9] have investigated the reaction between lithium metal and carbon monoxide using the technique of matrix isolation. The reaction was found to proceed through several steps. First, two isomers, LiCO and LiOC, are formed. Both compounds add another CO molecule to form two isomers of the LiC_2O_2 molecule. Finally, one of the LiC_2O_2 isomers reacts with the lithium to form the final product, $Li_2C_2O_2$. The experimental evidence reveals the existence of two distinct isomers of the $Li_2C_2O_2$ molecule. The two isomers have different frequencies of the C–O stretching. The authors of ref 9 hypothesized that the molecule that absorbs at 1279 cm^{-1} has a linear structure, whereas the less stable species with ν_{CO} = 1430 cm^{-1} has bridging lithium atoms. However, no further elucidation of the structure was possible based on the IR spectrum alone. Related experimental observations were also reported by Ayed et al.[10]

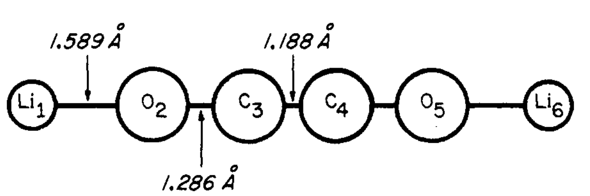


Figure 1. HF/6-311G*-optimized geometry of **1**.

In the present paper, we report on the results of ab initio calculations that rationalize the above experimental findings.

Computational Methods

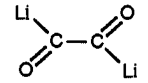
All calculations were performed on a FYRFOX VAX station running a VMS version of the GAUSSIAN88 package.[11] The geometries were optimized at the HF/6-311G*[12] level. The same level of theory was used for computation of the vibrational frequencies and the electron densities. The MP2/6-311G* energies were computed at the HF/6-311G* optimized geometries. The atomic charges were calculated within the GAPT formalism.[13] The critical points in the electron density were characterized with the aid of the EXTREM program of Bader.[14]

Results and Discussion

According to traditional ideas on bonding in organic molecules, one could expect two symmetrical isomers of the $Li_2C_2O_2$ molecule, namely the dilithium salt of dihydroxyacetylene (**1**) and the dilithiated glyoxal (**2**, either cis or trans). However, the results of our calculations indicate that structure **2** does not correspond to an energy minimum on the energy hypersurface. Instead, we find a minimum corresponding to a bicyclic structure (**3**) with four-membered rings, each involving a dicoordinate lithium atom.

$Li{-}O{-}C{\equiv}C{-}O{-}Li$

1



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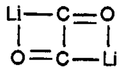

3

Existence of the nonclassical structure **3** is not surprising taking into account that the organolithium compounds often have unusual geometries that challenge traditional ideas of bonding.[15-17] Quite frequently, these unusual structures have lower energies than the classical ones. In the case of isomers **1** and **3**, we find that at the HF level they are almost equally stable (Table I). If the zero-point energy is included, the nonclassical structure becomes more stable than the linear one by about 1 kcal/mol. However, inclusion of electron correlation at the MP2 level favors isomer **1** by about 4 kcal/mol. This is consistent with the experimental observation that isomer **3** rearranges into isomer **1**.[9]

Existence of other possible isomers of the $Li_2C_2O_2$ molecule should be addressed here. Like **2**, the unsymmetrical structure LiO(Li)C=C=O was not found to be an energy minimum, despite extensive scans of the potential energy hypersurface. Other structures, such as those involving four-membered rings of the carbon and oxygen atoms coordinated with out-of-phase lithium atoms, if they exist, are expected to be much higher in energy than either **1** or **3**.

A thermal rearrangement of **1** to **3** is an electronically forbidden process, according to the orbital symmetries of the molecules. Therefore, to locate the respective transition state, one should use

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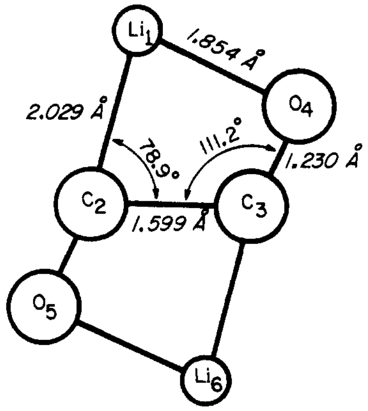

Figure 2. HF/6-311G*-optimized geometry of **3**.

a CAS SCF approach with at least two orbitals correlated. Calculations of several matrices of the force constants, necessary for such a search, is prohibitively expensive for the system under study. However, a clue to the possible energetics of the transition state is provided by HF/6-311G* calculations with the orbital occupancies frozen at the symmetries relevant to **1**. A stationary point with *two* imaginary frequencies is found to lie only ca. 6 kcal/mol above **1**. This indicates an extreme flatness of the potential energy hypersurface.

One may compare the geometry of **1** optimized at the HF level (Figure 1) with those of acetylene, methanol, and lithium hydroxide. The central carbon–carbon triple bond and the lithium–oxygen single bond have almost the same length as the respective bonds in acetylene and lithium hydroxide. However, the carbon–oxygen bond in **1** is substantially shorter than the single C–O bond in methanol. This indicates the presence of π-electron conjugation extended over the dihydroxyacetylene moiety. The geometry of **3** (Figure 2) is rather unusual. The carbon–carbon bond is longer than the usual single bonds. The carbon–oxygen bond is slightly longer than the C=O bond in formaldehyde. In order to decide on the presence of the Li–O and Li–C bonds in **3**, one has to first choose a particular definition of a chemical bond. Here, we employ the definition of a chemical bond based on Bader's theory of atoms in molecules, as it allows one to describe unequivocally any molecular structure in well-defined terms of topology.[18] According to this definition, existence of a bond is indicated by the presence of a bond path connecting the two atoms in question. Utilizing this criterion, we conclude that both the Li–O and Li–C bonds exist in **3**.

The GAPT atomic charges were repeatedly found[13,19] to be a convenient measure of the ionicity of chemical bonds. In **1**, the calculated charges (Table I) are consistent with the ionic character of the Li–O bonds. In **3**, the Li–O bond is found to be more covalent than in **1**. Finally, we comment on the calculated vibrational frequencies. As expected at the HF level, the calculated frequencies are overestimated compared to the experimental ones. Nevertheless, the C=O stretching frequency in **3** is found to be higher than in **1**. This is a direct consequence of the fact that the carbon–oxygen bond in **3** has a substantial double-bond character. The ratio of the calculated frequencies (1.16) is in semiquantitative agreement with the experimental one (1.12).

Conclusions

Our calculations explain the experimental findings on the isomers of the $Li_2C_2O_2$ molecule. Two structures are found to be minima on the energy hypersurface, in agreement with the experimental evidence. One may anticipate that further progress in experimental techniques will make determination of the geometrical structures of **1** and **3** possible. At the same time, one may expect more sophisticated treatment of electron correlation to bring the computed and observed vibrational frequencies into closer agreement.

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