



Research paper

The ability of a tetrel bond to transition a neutral amino acid into a zwitterion

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HIGHLIGHT

- A π -tetrel bond is formed between the C/Si atom of F₂CO/F₂SiO and the carboxyl O atom of glycine.
- The Si...O tetrel bond is especially strong, approaching the characteristics of a covalent bond.
- The -COOH proton can be transferred to the -NH₂ group by the Si...O tetrel bond.

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ABSTRACT

The interaction between glycine and F₂CO/F₂SiO occurs through the formation of a π -tetrel bond between the C/Si atom and a carboxyl O atom. The interaction energy is some 20 kJ/mol for the C...O tetrel bond, but exceeds 300 kJ/mol for Si...O. As part of the latter complexation process, the proton engaged in the intramolecular OH-N H-bond is transferred across to the N, forming a zwitterion. This Si...O tetrel bond is more effective in inducing this proton transfer than is placement of the glycine in an aqueous medium, complexation with an anionic BH₄⁻, or adding an electron to the glycine.

1. Introduction

Noncovalent interactions including the tetrel bond have attracted increasing attention because of their extensive applications in crystal engineering [1,2], supramolecular chemistry [3–5] and chemical reactions [6,7]. Their influence in biological systems [8] is profound and our understanding of their behavior is necessary for elucidation of biological mechanisms. For example, hydrogen bonding plays an important role in maintaining the three-dimensional structures of biomolecules including peptides [9], proteins [10], carbohydrates, and nucleic acids [11]. A recent study showed that H-bonding is of great importance in controlling the degradation of radical cations of DNA bases [12]. It is well known that intramolecular proton transfer is one of the simplest and most important reactions in biochemistry and is a key process in many biological systems [13–15]. There are many possible protonation sites in biomolecules, and protons can be transferred from one site to another, which is a basic phenomenon in biological reactions [16]. Work has also been dedicated to hydrogen bonds and proton transfer in electronic excited states, including photophysical processes

and photochemical reactions involving proton transfer [17–24].

Amino acids are the building blocks of proteins [25,26], and elucidating their configuration is correspondingly important. As the simplest amino acid, glycine is often taken as a model, with extensive applications in food, medicine, enzyme catalysis, feed, and the chemical industry [27]. Polyglycine is mainly present in silk fibroin in the form of a β -sheet [27] and is a basic precursor for the synthesis of proteins, nucleic acids and lipids. The crystal structure of glycine was probed [28] as early as 1939, and its morphology was elaborated [29]. Different forms of amphoteric glycine ions have different properties [30], resulting in a wide variety of functions [31]. Glycine and its protonated species have been thoroughly investigated by experimental and theoretical methods [31–38]. Although amino acids exist in their neutral forms in the gas phase, zwitterions predominate in aqueous solution. There are many factors that influence structural changes of glycine. For example, H-bonding between the BH₄⁻ anion and glycine has a strong effect on glycine's configuration [39]; solvation [40,41] and ionization [42] also affect its structure.

The tetrel bond is a noncovalent bond involving atoms of group IV

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[43], with similarity to H-bonding, and numerous studies have accordingly focused on the structures, properties, strength, nature and applications of tetrel bonds [44–52]. In a recent study, our own group explored the effect of tetrel bonding on the strength of an intramolecular hydrogen bond in malondialdehyde (MDA) [53]. The π -tetrel bond strengthens/weakens the MDA internal H-bond when the bond is formed to the hydroxyl/carbonyl group of MDA, leading to inhibition/promotion of the proton transfer [53]. There is thus reason to inquire as to whether a similar sort of tetrel bond can affect, or even induce, intramolecular proton transfer in glycine?

This work thus reports the results of quantum calculations of the intramolecular OH...N H-bond within glycine. A transfer of the bridging proton will transform the neutral glycine into a zwitterion. The F₂TO molecule, with T = C and Si, has been shown earlier [46,47,53] to be a potent tetrel bonding species via the π -hole that lies above its molecular plane. F₂CO and F₂SiO were each allowed to interact with glycine, scrutinizing the heterodimer potential energy surface for all possible minimum energy structures. For each structure, the preferred position of the bridging proton on the internal OH...N H-bond was identified, along with the energy barrier which must be surpassed in order for the neutral form to transit to the zwitterion. These effects were then compared to those of the BH₄⁻ anion which had been shown previously to affect proton position. Solvation effects were also considered as highly polar solvents are known to favor zwitterion formation.

2. Computational methods

The Gaussian 09 program [54] was used to perform the optimization and frequency calculations at the MP2/aug-cc-pVTZ level. The absence of any imaginary frequencies verifies the optimized structures are true minima. Interaction energies were calculated using the supermolecular approach, in which the geometries of monomers in the complexes were taken as a point of reference. This quantity was corrected for the basis set superposition error (BSSE) by the counterpoise method of Boys and Bernardi [55]. Solvent (H₂O) calculations were carried out by means of the polarizable continuum model (PCM) [56].

The second-order perturbation energy between pairs of orbitals was obtained at the HF/aug-cc-pVTZ level by the natural bond orbital (NBO) method [57]. Molecular electrostatic potentials (MEPs) on the 0.001 au contour of electron density were calculated at the MP2/aug-cc-pVTZ level using the wave function analysis-surface analysis suite (WFA-SAS) program [58]. Topological analyses were performed using the atoms in molecules (AIM) methodology [59]. AIM 2000 software [60] was used to calculate topological parameters including the electron density, its Laplacian, and energy density at bond critical points (BCPs). Intrinsic reaction coordinate (IRC) calculations connected each transition state (TS) to its corresponding reactants and products.

3. Results and discussion

The four different configurations of glycine monomer are illustrated in Fig. 1, along with their relative energies. G''' is the most stable geometry, wherein the OH of the COOH group is cis to the carbonyl O and the NH₂ protons lie above and below the N–C–C–O molecular plane. G lies 1.35 kJ/mol higher in energy, differing from G''' in that the OH is trans to the carbonyl O. 3.42 kJ/mol higher is the G'' structure where the OH is again cis to C=O but the NH₂ protons lie roughly in the molecular plane. G' is least stable with its trans OH and position of the NH₂ protons toward the OH. Although known to be neutral in the gas phase, as in the four configurations in Fig. 1, the OH proton transfers to the NH₂ group in the aqueous phase, leading to the well known zwitterionic form. Since this proton transfer can only occur through a cis structure, and as G' is 23 kJ/mol less stable than G, it is the latter configuration that is chosen as the focus of this study of proton transfer.

Previous calculations have shown a number of external influences

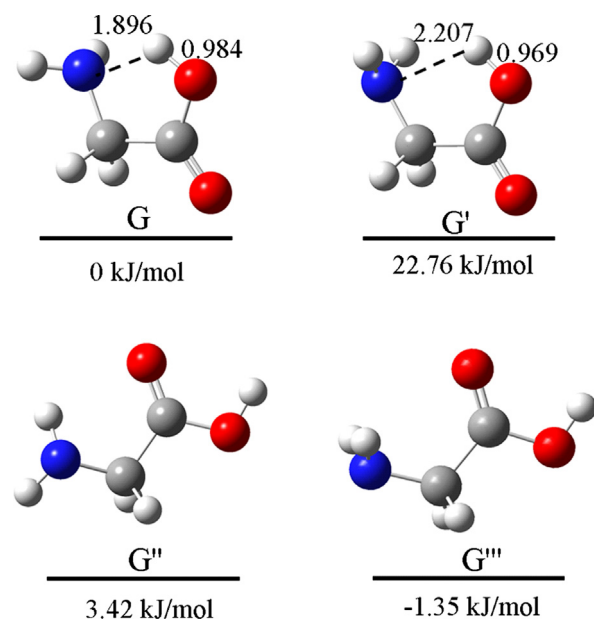


Fig. 1. . The four configurations of glycine; distances in Å.

can cause the proton transfer to a zwitterionic form. Inclusion of a number of water molecules, for example, preferentially stabilizes the zwitterion through the intermediacy of their H-bonds [61–63]. Another prior work had concluded that even a single intermolecular H-bond to the NH₂ group of G can promote this transfer [39]. Another work [53] demonstrated that a tetrel bond to F₂TO (T = C, Si) induces a proton transfer within malondialdehyde (MDA). The question then arises as to whether this same sort of tetrel bond might similarly cause a proton transfer in glycine.

As a preliminary step in understanding any such tetrel bond, the molecular electrostatic potential (MEP) of G, and both F₂CO and F₂SiO are pictured in Fig. 2. Negative (blue) regions are found on both the hydroxyl and carbonyl O atoms, with the latter more negative. There are positive red areas (π -holes) above and below the molecular plane of F₂TO; the values of the maximum indicated in Fig. 2 make the π -hole above the Si atom twice as intense as those above the C atom. Based on these patterns, one can certainly envision a π -hole tetrel bond between either O atom of G and the π -hole of F₂TO. However, attempts to form a tetrel bond with the hydroxyl O failed; it is only the carbonyl O that engages in such a bond.

When the F₂TO π -hole approaches the carbonyl O atom, three structures are obtained, denoted as a, b, and c in Fig. 3. The a structure contains a “pure” tetrel bond, i.e. no significant secondary interactions. The b dimer also contains a pair of CH...F H-bonds, while c supplements the primary tetrel bond with a pair of CH...O H-bonds. Whether T = C or Si, it is the c configuration that is most stable, followed by b and then by a. There is a sizable difference between C and Si energetics. The interaction energies for T = Si vary from 175 to 320 kJ/mol while the C values are all less than 25 kJ/mol. Along with the stronger Si tetrel bonds is a much shorter R(T...O) distance: 1.8 Å for Si vs 2.6 Å for C.

The tetrel bond formation causes an elongation of the internal O–H bond length in G. Equaling 0.984 Å in the G monomer, it stretches slightly by 0.002–0.006 Å for the F₂CO complexes. But this stretch is magnified in the stronger Si tetrel bonded complexes. Indeed, r(OH) is considerably longer than r(NH) in both the b and c complexes of F₂SiO. The short r(NH) distances of less than 1.08 Å, with r(OH) ~ 1.6 Å, can be characterized as a full-fledged proton transfer from O to N.

The idea that a proton transfer has occurred is further bolstered by AIM topological parameters of the electron density. The quantities associated with the NH and OH bond critical points are displayed in Table 1. The covalent OH bond in monomer G is clear by the large

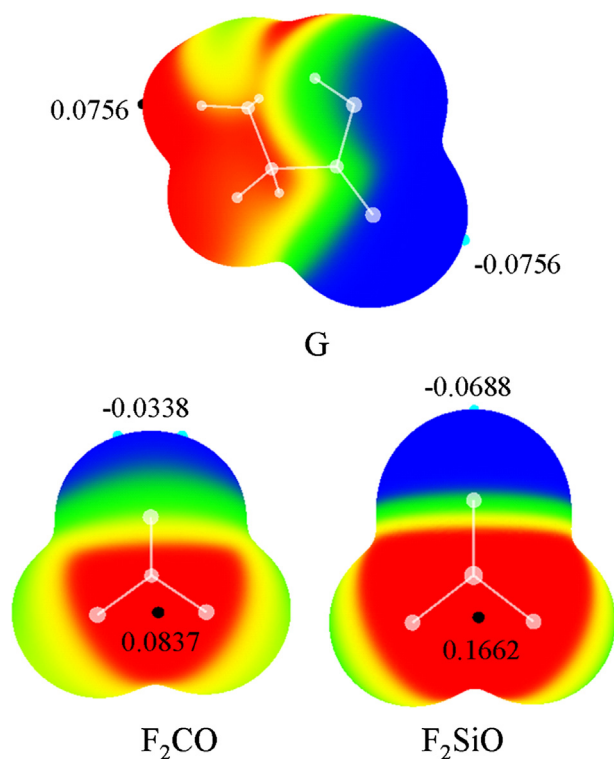


Fig. 2. MEP maps of monomers. Color ranges are: red, greater than 0.03; yellow, between 0.03 and 0; green, between 0 and -0.03 ; blue, less than -0.03 . Values of the MEP at maxima and minima on the surface are indicated in au. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

values of ρ , $\nabla^2\rho$, and H in the corresponding columns of the first row of Table 1, dwarfing the NH values preceding them. The density Laplacian is negative for OH, and positive for NH, consistent with their respective covalent and noncovalent character [64]. This pattern continues for all of the complexes, with the exception of G-F₂SiO-b and G-F₂SiO-c in the last two rows. It is here that the order reverses and the AIM quantities are much larger for NH than for OH, and the OH Laplacian becomes positive, while that for NH turns negative.

From a more subtle perspective, the formation of the tetrel-bonded complexes can be seen to strengthen the internal OH \cdots N H-bond, even when no transfer occurs. Skimming down the columns of Table 1 shows small increases in the N–H parameters, coupled with small decreases in the corresponding O–H quantities. This same pattern is observed for the NBO interorbital charge transfers in the last column of Table 1. These entries refer to the $Lp(N) \rightarrow \sigma^*(O-H)$ for the OH \cdots N H-bonded cases, and $Lp(O) \rightarrow \sigma^*(N-H)$ for the last two rows after the proton has transferred to the N. Note that there is a strong NH \cdots O H-bond after the transfer has occurred.

While the interaction energies shown in Fig. 3 are quite large, it should be stressed that this quantity refers to the interaction between monomers that have already been distorted into the geometries they adopt within the complex. As such, there is a certain amount of monomer deformation energy that must be overcome before this encounter can occur. These deformation energies are listed in the last column of Table 2, where it may be seen that they are quite large for the F₂SiO complexes, as much as 155 kJ/mol. Much of this distortion is associated with loss of planarity in the F₂SiO monomer, transitioning toward the pyramidal structure necessary to engage in the very strong tetrel bond. When these deformation energies are subtracted from E_{int} , one has the binding energies E_b , that take the system from a pair of isolated monomers in their optimum geometries, to the complexes indicated. E_b is less than 24 kJ/mol for the F₂CO complexes but in the

128–167 kJ/mol range for F₂SiO.

Whereas the global minimum may place the proton on either the N or the O, there may be a secondary minimum on the potential energy surface corresponding to its placement on the other atom. In the case of glycine itself, there is no such second minimum, as the OH \cdots N structure represents the only minimum. The same is true if G engages in a complex with F₂CO. Upon complexation with F₂SiO, the result depends upon the specific structure. Within the context of the a and b structures, the OH \cdots N geometry is considerably more stable than O \cdots NH, by 16.5 and 6.2 kJ/mol, respectively. Indeed, the well containing the secondary minimum is so shallow that it is difficult to isolate the transition state separating them, so a spontaneous decay to OH \cdots N is anticipated. In the c geometry, on the other hand, the two minima are very similar in energy, with NH \cdots O the more stable, but by only 0.3 kJ/mol. The proton transfer would be nearly spontaneous since a barrier of only 8.4 kJ/mol must be surmounted, as shown in Table 3.

It is well known that a polar environment such as an aqueous medium favors a zwitterionic form of an amino acid such as glycine. And indeed, this influence was clear when G was placed in a PCM dielectric continuum model of water, where the solvation causes the appearance of a second minimum in the proton-transfer potential, corresponding to the zwitterionic form. The zwitterion is 5.8 kJ/mol higher in energy than the neutral OH \cdots N configuration, separated from it by a barrier of 17.1 kJ/mol. But what is striking is that even solvation by water exerts less of a force to push the proton from O to N, than does a single tetrel-bonding F₂SiO which makes the zwitterion the preferred structure, and reduces the transfer barrier.

In a similar vein, a prior theoretical study [39] on the intramolecular proton transfer in glycine considered the influence of a BH₄[−] anion which engages in a dihydrogen bond with the NH proton in the glycine molecule. By enhancing the ability of the N atom to accept a proton, this anion facilitated the transfer of the $-\text{COOH}$ proton to the N atom. The question thus arises as to whether such a dihydrogen bond exerts a stronger influence on the proton transfer than does the tetrel bond discussed above. In the BH₄[−] case, the NH \cdots O configuration was calculated to be less stable than OH \cdots N by 3.1 kJ/mol, as opposed to the tetrel-bonded G-F₂SiO-c where it is the former proton-transferred structure that is more stable. Moreover, the transition state is much higher for BH₄[−], 13.8 kJ/mol. The greater ability of the neutral tetrel-bonding F₂SiO to facilitate the proton transfer, when compared to a full-fledged anionic BH₄[−] is a further testament to the power of this sort of interaction to induce structural changes.

It is interesting to consider how the process might be affected by the addition of an excess electron. Optimization of the glycine anion found that the OH \cdots N configuration is more stable than NH \cdots O by 22 kJ/mol. IRC identification of the transition state to proton transfer in this anion indicates an energy barrier of 24.1 kJ/mol. Thus while the anion does appear to have two separate minima, the energy barrier is higher than that associated with the tetrel bond or placing the system within the confines of aqueous solution.

4. Conclusions

In summary, both F₂CO and F₂SiO can engage in a complex with glycine, the latter being much stronger than the former. The complexes are held together primarily by a π -tetrel bond wherein the glycine O atom lies above the F₂TO molecular plane. The Si \cdots O tetrel bond is especially strong, approaching the characteristics of a covalent bond. In one of the three interaction modes with F₂SiO, the $-\text{COOH}$ proton can be transferred to the $-\text{NH}_2$ group, forming a zwitterion of energy no higher than the normal OH \cdots N form. The two wells in the proton transfer potential are separated by an energy barrier of 8 kJ/mol. This tetrel bond with F₂SiO is more effective in promoting the proton transfer from O to N than is (i) placement within the context of aqueous medium, (ii) complexation with a BH₄[−] anion, or (iii) adding an extra electron to the glycine unit.

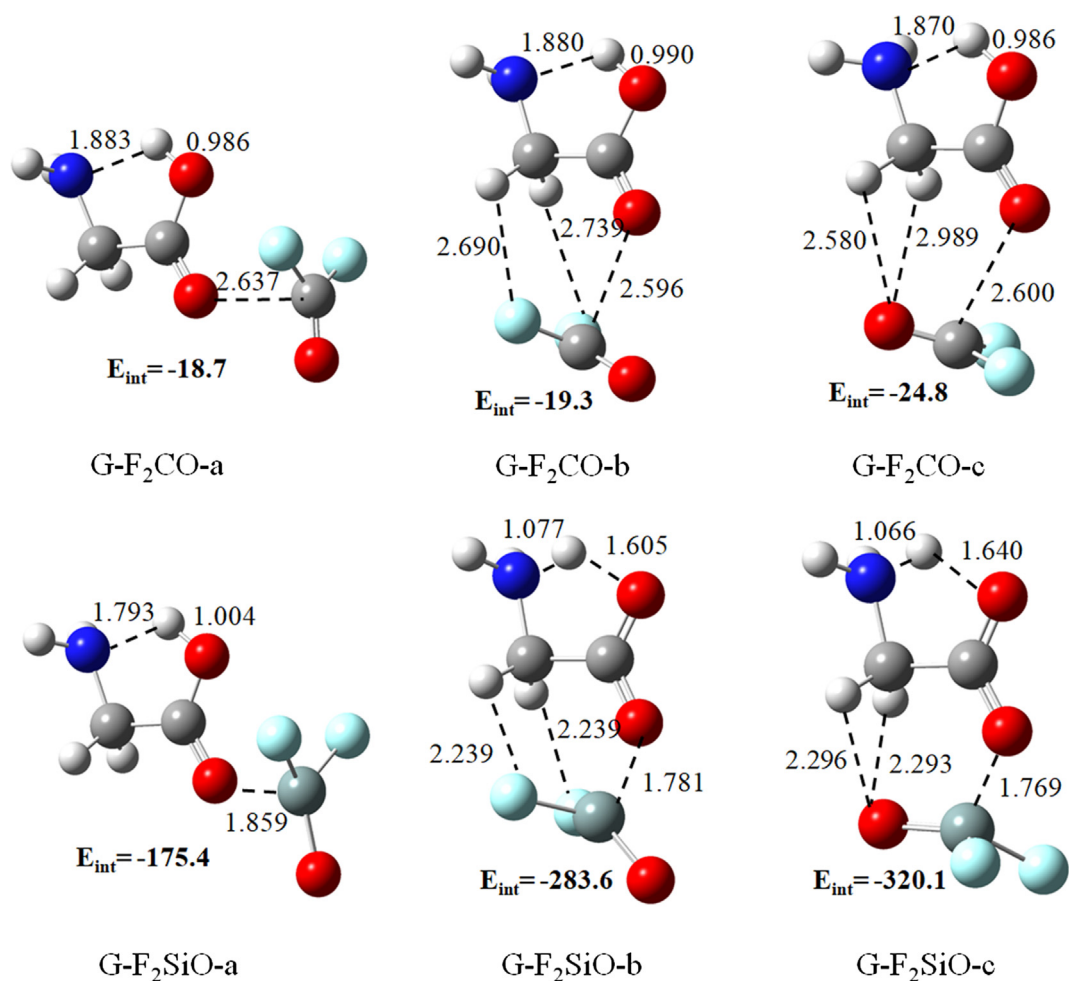


Fig. 3. Structures of three types of complexes between glycine and F₂TO. Interaction energies E_{int} in kJ/mol, and distances in Å.

Table 1

Electron density (ρ , au), its Laplacian ($\nabla^2\rho$, au) and energy density (H , au) at the N–H and O–H BCPs as well as second-order NBO perturbation energy (E^{2a} , kJ/mol) in the G monomer and its complexes with F₂TO.

	$\rho_{\text{N-H}}$	$\nabla^2\rho_{\text{N-H}}$	$H_{\text{N-H}}$	$\rho_{\text{H-O}}$	$\nabla^2\rho_{\text{H-O}}$	$H_{\text{H-O}}$	E^{2a}
G	0.036	0.115	-0.002	0.347	-2.705	-0.737	53.55
G-F ₂ CO-a	0.037	0.115	-0.003	0.344	-2.686	-0.731	58.77
G-F ₂ CO-b	0.037	0.113	-0.003	0.340	-2.642	-0.719	72.61
G-F ₂ CO-c	0.038	0.116	-0.003	0.343	-2.681	-0.730	62.49
G-F ₂ SiO-a	0.046	0.114	-0.008	0.322	-2.520	-0.686	99.28
G-F ₂ SiO-b	0.291	-1.919	-0.519	0.065	0.153	-0.018	161.81
G-F ₂ SiO-c	0.301	-2.012	-0.542	0.059	0.158	-0.014	133.17

^a E^{2a} corresponds to the orbital interaction of $\text{Lp}(\text{O}) \rightarrow \sigma^*(\text{N-H})$ in G-F₂SiO-b and G-F₂SiO-c but $\text{Lp}(\text{N}) \rightarrow \sigma^*(\text{O-H})$ in other cases.

Table 2

Interaction energy (E_{int}), binding energy (E_{b}) and deformation energy (DE), all in kJ/mol.

	E_{int}	E_{b}	DE
G-F ₂ CO-a	-18.70	-17.93	0.77
G-F ₂ CO-b	-19.30	-13.81	5.49
G-F ₂ CO-c	-24.78	-23.60	1.18
G-F ₂ SiO-a	-175.42	-127.74	47.68
G-F ₂ SiO-b	-283.58	-128.90	154.67
G-F ₂ SiO-c	-320.10	-166.75	153.36

Table 3

Energy difference ΔE of NH-O zwitterion configuration relative to OH-N and energy of transition state for proton transfer E^\ddagger , all in kJ/mol.

	ΔE	E^\ddagger
G-F ₂ SiO-c	-0.34	8.35
G(aq)	5.79	17.14
G-BH ₄ ⁻	3.14	13.81
G-e	22.00	24.07

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

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