Biradicals

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Unusual Inorganic Biradicals: A Theoretical Analysis**

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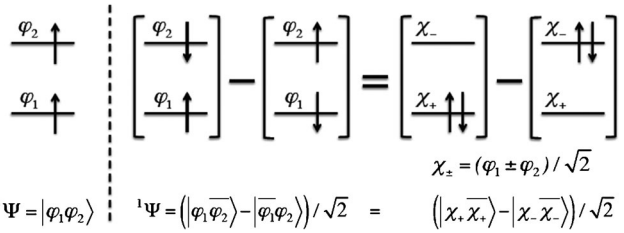
According to the International Union of Pure and Applied Chemistry (IUPAC) "Gold Book",[1] a biradical system is defined as "an even-electron molecular entity with two (possibly delocalized) radical centers which act nearly independently of each other".[2,3] The lowest-energy triplet state of a biradical, the same source adds, lies below or at most only a little above its lowest singlet state. Typical examples of stable biradicals consist of organic molecules in which the two lone electrons are well-separated from each other.[4,5] Biradicals have been identified as transient intermediates in photocycloaddition reactions,[5,6] a fact that makes their isolation difficult. A typical example of an organic biradical is trimethylenemethane (TMM), $C(CH_2)_3$, for which ESR measurements suggested a triplet ground state of D_{3h} symmetry[7] and a singlet first excited state[8] of C_{2v} symmetry as a result of a Jahn–Teller distortion lying (16.1 ± 0.1) kcal mol^{-1} above it.[9] The biradical character of TMM and its derivatives has been exploited in cycloaddition reactions forming highly complex molecular structures.[10] Recently, the role of the Criegee biradical (H_2COO) in helping offset global warming by breaking down sulfur dioxide and nitrogen dioxide in the atmosphere has been reported.[11] Among the inorganic biradical species, ozone (O_3) has long been considered one of the prototype candidates from the early theoretical work[12–14] until recent debates[15,16] regarding its biradical character.

From a quantum mechanical viewpoint, unpaired electrons occupying two different orbitals φ_1 and φ_2 can form either a triplet $^3\Psi = |\varphi_1\varphi_2\rangle$ or a singlet $^1\Psi = (|\varphi_1\overline{\varphi_2}\rangle - |\overline{\varphi_1}\varphi_2\rangle)/\sqrt{2}$ state, where $\varphi_k(\overline{\varphi_k})$ is used for spin "up"("down"), $\uparrow(\downarrow)$,[17] and the rest of the doubly occupied orbitals are omitted (Scheme 1). The singlet wavefunction can



Scheme 1. Triplet ($^3\Psi$) and singlet ($^1\Psi$) wavefunctions of unpaired electrons occupying two different orbitals φ_1 and φ_2.

be recast as $^1\Psi = (|\chi_+\overline{\chi_+}\rangle - |\chi_-\overline{\chi_-}\rangle)/\sqrt{2}$ in terms of $\chi_\pm = (\varphi_1 \pm \varphi_2)/\sqrt{2}$. In this expression, the second term represents a strong correlation that changes the closed shell structure of the first term into a full biradical.

The leading terms in general multi-reference configuration interaction (MRCI) wavefunctions of a singlet electronic state typically have the form

$$^1\Psi = (c_1|\chi_+\overline{\chi_+}\rangle - c_2|\chi_-\overline{\chi_-}\rangle)\Big/\sqrt{c_1^2 + c_2^2},$$

where $c_1 > c_2$. In this case, the quantity

$$\beta = 2c_2^2/(c_1^2 + c_2^2)$$

can be taken[14,18] as a measure of the biradical character of the singlet electronic state. Such wavefunctions contain of course a larger number of terms, but for the purpose of the present analysis the contribution of terms with coefficients $c_k < 0.1$ will be neglected. This definition of β is consistent with the quantum mechanical association of probability with the square of the corresponding coefficient, and it encompasses the two extremes of closed-shell molecules ($c_2 = 0$, $\beta = 0$) as well as pure biradicals ($c_2 = c_1$, $\beta = 1$).

Focusing on the O_3-homologous YX_2 series, namely triatomic molecules with 18 valence electrons, we consider the molecules $(CX_2)^{2-}$, $(NX_2)^-$, X_3, OX_2, $(FX_2)^+$, that is, Y = C, N, O, F and X = O, S, Se, Te, Po being the terminal atoms. For these systems, the geometries were optimized at the complete active space self-consistent field (CASSCF) level of theory[19–22] with the cc-pVTZ basis set[23] and the expansion coefficients were obtained via internally contracted MRCI (*ic*MRCI) calculations[24,25] with the MOLPRO suite of codes.[26] For X = Se, Te, Po, the cc-pVTZ-PP basis set[27] was employed, producing near-identical results with those obtained for Se with the cc-pVTZ set. The geometrical parameters at the optimum CASSCF geometries, the *ic*MRCI energies and corresponding coefficients are listed in the Supporting Information, Table S1. All of these geometries correspond to minima on the potential energy surface, as

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confirmed by the fact that the Hessian index is zero (all frequencies are real). At the equilibrium geometries (C_{2v} symmetry) of all molecules in the series, there are four electrons in the three valence out-of-plane π-orbitals (π_0, π_1, and π_2), as described earlier for O_3 and OS_2.[16] The π_0 orbital is mostly located on the central atom, whereas the other two (π_1, π_2) are mostly localized on the terminal X atoms. The wavefunction, considering only the π-electrons and ignoring the smaller components of the MRCI vector, has the form $^1\Psi = \left(c_1|\pi_0^2\pi_1^2\rangle - c_2|\pi_0^2\pi_2^2\rangle\right)/\sqrt{c_1^2+c_2^2}$, which falls under the category described above. The biradical character β (evaluated using the *ic*MRCI coefficients) for the five series of molecules is shown in Figure 1 (see also the Supporting Information, Table S1).

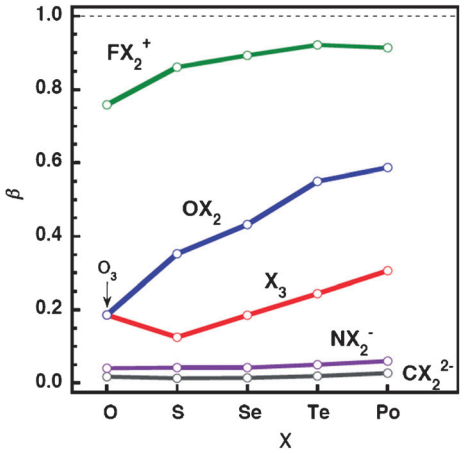

Figure 1. Biradical character β for the $(CX_2)^{2-}$, $(NX_2)^-$, X_3, OX_2, $(FX_2)^+$ series, where X = O, S, Se, Te, Po.

Independently of the central atom, the biradical character β increases monotonically within each series as the terminal atom X moves down the periodic table. The physical reason behind this trend is that the larger X becomes, the further the two terminal atoms are, and this facilitates the better separation of the two electrons occupying the π_1 and π_2 orbitals located on these terminal X atoms. This is consistent with the corresponding increase in the Y–X bond length (Supporting Information, Table S1). The exception to this general trend is in the X_3 series going from O_3 to S_3, where β decreases. An explanation for this behavior, based on the charge transfer from the central atom to X owing to the difference in the relative electronegativities, has been previously discussed.[16]

The biradical character also increases across the series from C to F. Here, the progressive enhancement of the electronegativity of the central atom draws increasing amounts of electron charge out of the π-bonds and away from the end atoms towards the central atom. This charge shift progressively weakens the π-bonds and brings the π-electron occupancy of the central atom closer to 2. The π-orbitals of the two end atoms, on the other hand, are getting closer to being singly occupied so that the end atoms acquire increasing radical character. The increase from O to F is particularly dramatic. For the members of the FX_2^+ series, the orbital π_0 is roughly equal to the p_π orbital of fluorine ($\pi_0 \approx 0.97\, p_\pi$), and the large electronegativity of fluorine maintains the double occupancy of this orbital. For this reason, the members of the FX_2^+ series have a much larger biradical character than the other series (Figure 1). In the case of FPo_2^+, $c_1 = 0.6957$, $c_2 = -0.6374$ (with the rest of the icMRCI coefficients < 0.06), yielding $\beta = 0.913$, a value that approaches the perfect biradical ($\beta = 1$) case. The small drop in β from FTe_2^+ ($\beta = 0.921$) to FPo_2^+ ($\beta = 0.913$) is probably due to the use of the CASSCF geometries for the *ic*MRCI calculations, as the biradical character increases monotonically when CASSCF coefficients are used (Supporting Information, Table S1). However, the difference in the values of β obtained using the CASSCF and *ic*MRCI expansion coefficients is quite small ($\lesssim 0.01$).

To put the results for the biradical character of the YX_2 series into perspective with well-known organic biradical species, we performed analogous calculations for TMM [$C(CH_2)_3$]. Our calculations confirm that at the equilibrium geometry of TMM the four electrons of the π-system are distributed within the lowest three π-orbitals in the following three electronic states:

$$\Psi(^3A_2'') \approx 0.964|\pi_0^2\pi_1^1\pi_2^1\rangle,$$

$$\Psi(^1A_1) \approx 0.702|\pi_0^2\pi_1^2\rangle - 0.684|\pi_0^2\pi_2^2\rangle, \text{ and}$$

$$\Psi(^1B_2) \approx 0.685|\pi_0^2\pi_1\overline{\pi_2}\rangle - 0.685|\pi_0^2\overline{\pi_1}\pi_2\rangle.$$

The ground state (first wavefunction) is indeed a triplet, the second wavefunction has $\beta = 0.97$, suggesting a near-perfect singlet biradical state, whereas the last wavefunction corresponds to a regular open-shell singlet (see Scheme 1).

Focusing on the singlet states of the 24-electron XO_2 series, we consider molecules with two oxygen atoms and a moiety X that is isoelectronic to oxygen, that is, X = CH_2, NH, O, F^+. The relative energies [eV] and values of β of the different isomers within each series are shown in Figure 2.

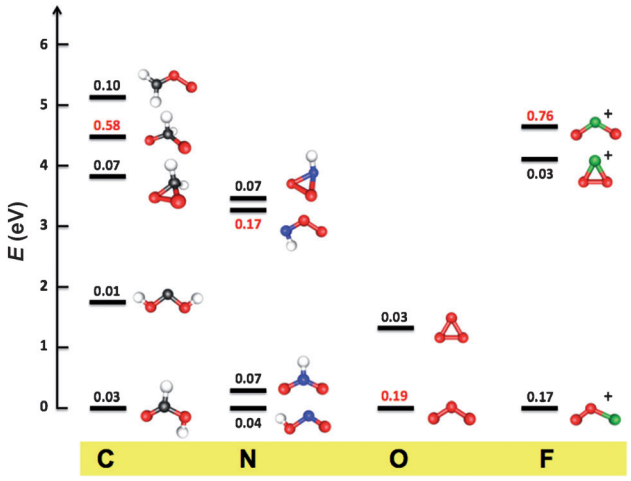

Figure 2. Isomers, their energy separation [eV], and biradical character (β) of the 24-electron XO_2 series, X = CH_2, NH, O, F^+. The largest value of the biradical within each series is indicated in red.

Apart from O_3, the ground state of all species has lower symmetry, that is, the OXO structure with C_{2v} symmetry (albeit a local minimum) is not the most stable form. The largest biradical character in this series is associated with the open-form (no bond between the terminal O atoms) OFO^+ ($\beta = 0.76$) and the next one is that of the open-form $O(CH_2)O$ ($\beta = 0.58$). The former case was discussed earlier, while the large biradical character of the latter molecule is a result of the fact that the two hydrogen atoms linked to carbon reserve the p_π orbital of C for the C–H bonds and restrict the two remaining π-electrons to either of the two terminal oxygen atoms. The open structure of O_3, also discussed earlier, has $\beta = 0.19$, whereas the smaller biradical character in the series is found in HNOO ($\beta = 0.17$). As expected, the lowest-energy isomers in the C and N series, formic acid (HCOOH) and nitrous acid (HONO), have a negligible biradical character ($\beta < 0.05$). The Criegee "biradical" has a value of β that is quite low on the scale ($\beta = 0.10$).

As regards the ring conformations of the above series, they all have a negligible biradical character ($\beta < 0.08$) as anticipated by the formation of a bond between the terminal atoms. They are lower in energy when compared to the open-form OXO (C_{2v}) isomers for FO_2^+ and H_2CO_2, and higher for O_3 and HNO_2. In all four cases, there exists an energy barrier when moving from the open-form to the ring structures.[28,29] Ideally, this barrier would be smaller if there were two lone electrons isolated in each of the two terminal oxygen atoms that could facilitate the O–O bonding. It would therefore be expected that the height of the energy barrier (Supporting Information, Table S2) to vary inversely with the biradical character of the molecule in its open-form OXO geometry.

As regards the triplet state of the open-form OXO, ${}^3\Psi \approx |\pi_0^2\pi_1^1\pi_2^1\rangle$, this is always higher in energy than the corresponding singlet, but for FO_2^+ and H_2CO_2 (due to their large biradical character) it is much closer to the singlet state, in accordance to the definition provided by IUPAC. The singlet–triplet energy splitting of the four OXO species as a function of $1/\beta$ (Figure 3) follows a linear trend for the four species considered (the correlation coefficient is $R = 0.9936$).

In summary, we have identified several triatomic inorganic biradical ions in the FX_2^+ series with X = O, S, Se, Te, and Po being the terminal atoms, that have unusually high biradical characters ($0.76 < \beta < 0.92$). The last two in the series, FTe_2^+ and FPo_2^+, have values of 0.92 and 0.91 on the biradical scale, similar to the one of a classic organic biradical, such as trimethylenemethane ($\beta = 0.97$). In contrast, previous prototypes of inorganic biradicals such as O_3 have a value of just 0.19 on the biradical scale. This value corresponds to the value of 0.44 in reference [16] because there the biradical character β was defined as $\sim c_2$ whereas here we have defined it as $\sim c_2^2$. The S–T splitting was found to vary linearly with the inverse of the biradical character for various members of the 24-electron homologous XO_2 series with two terminal oxygen atoms and X isoelectronic to oxygen, that is, X = CH_2, NH, O, F^+, the singlet (S) state lies below the triplet (T) state.

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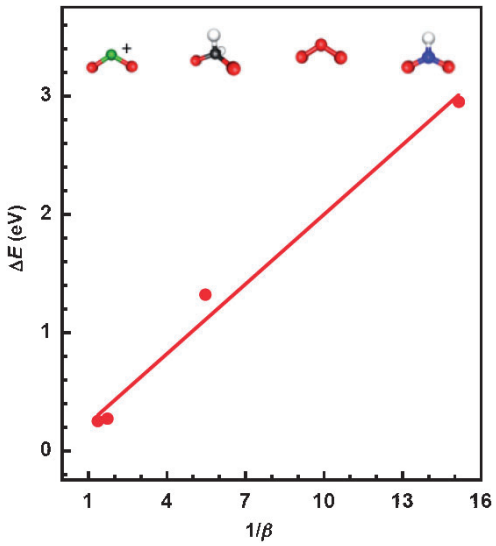

Figure 3. Singlet–triplet (S–T) splitting as a function of $1/\beta$ for the FO_2^+, CH_2O_2, O_3, and NHO_2 open species.

Keywords: biradical character · Criegee biradicals · ozone · singlet–triplet splitting · unpaired electrons

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