

C₂ Revisited: experiment and theory

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Carbon–carbon bond is the backbone of organic chemistry and carbon materials, and yet the details of the simplest system that exhibit a C–C bond, C₂, is only slowly unravelling. Despite its existence everywhere, characterization of C₂ has been a formidable issue. C₂ generated in the gas phase reacts as though it is a mixture of singlet dicarbene and a triplet diradical, the former in larger concentration^{1–4}. Recently, Miyamoto *et al.*⁵ presented a classical synthesis of C₂ in a flask to further understand the structure and reactions of C₂. The electronic structure of C₂ has also been debated intensely by theoreticians; it is recognized as the most complex homodiatom of the second row of the periodic table of elements⁶. Description of C₂ as a singlet diradical with a weak 4th bond is gaining acceptance⁷. Bhattacharjee *et al.*⁸ recently presented an analysis of the nature of binding in C₂ by studying different excited states of C₂, bringing the issue into focus again.

A brilliant strategy of using a super leaving group in a hypervalent iodane compound enabled Miyamoto *et al.*⁵ to achieve their chemical synthesis of C₂ (Figure 1). Addition of tetra-*n*-butylammonium fluoride led to the displacement of SiMe₃ and subsequent elimination of iodobenzene generating C₂, evidenced by the evolution of acetylene. However, the *in situ* generated C₂ in solution did not react with unsaturated compounds such as acetone, styrene, etc. This clearly distinguishes the chemically synthesized C₂ from that is generated from gas phase dissociation or arc synthesis which reacted with unsaturated systems even at very low temperatures. On the other hand, C₂ generated in solution reacted with 9,10-dihydroanthracene to give anthracene and acetylene, clearly supporting a singlet-biradical description for C₂. Galvenoxyl radical gives monogalvenoxyl acetylene (traces of digalvenoxyl acetylene were also found) with C₂. This is attributed to the higher reactivity of the mono radical relative to C₂ which has a weak σ -bond according to Valence Bond theoretical studies. The C₂ generated here also leads to fullerene, graphite and carbon nanotubes, giving important support for the mechanistic

steps involved in carbon cluster chemistry.

Valence Bond theory had concluded that C₂ is quadruply bonded, with weak σ -bonds. In contrast, MO theory which correctly predicted the bonding description of N₂ and O₂, attributes at its simplest level a double bond to C₂, more like a dicarbene^{9,10}. The basis for this argument is seen in Figure 2 *a* for N₂ which has a triple bond. Experimentally it has been shown that the HOMO of N₂ ($3\sigma_g$) corresponds to the σ -bond^{11,12}. Removal of two electrons as in C₂ leads to an occupancy devoid of the σ -bond and two π -bonds remain (Figure 2 *b*). The single determinant (one configuration) approach works reasonably well for N₂ and O₂. However, C₂ has several low lying vacant levels, an indicator that a multi-configuration approach is needed for the proper description of the singlet ground state. There should be several other electron configurations that contribute to the

ground state. While there had been previous studies at various levels, Bhattacharjee *et al.* provide a very novel approach, with the hypothesis that if there is a bound state (a minimum in the PEC) there must be a bond. As its corollary, if an excited state PEC obtained by pushing an electron to a higher level shows an unbound state, the initial electronic state must have had a bond. For example, the σ -bond in H₂ is broken (PEC is purely dissociative) when one electron is excited from the σ to σ^* level ($^3\Sigma_u^+$). In a triple bonded system such as N₂, it is necessary to excite three electrons to populate three vacant antibonding levels ($^7\Sigma_u^+$) to get to a dissociative PEC, indicating that there are three bonds in ground state of N₂. The authors use this approach for studying the bond order of C₂. Thus, the electronic structure of the ground state as well as various excited states are studied using a multi-configuration approach so that the

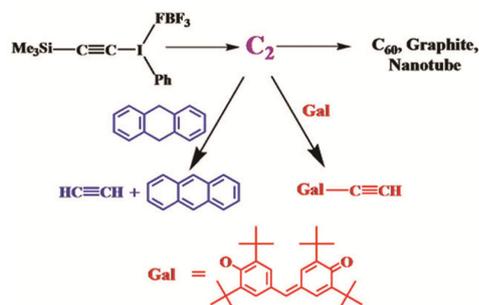


Figure 1. Schematic representation of the generation and reactions of C₂.

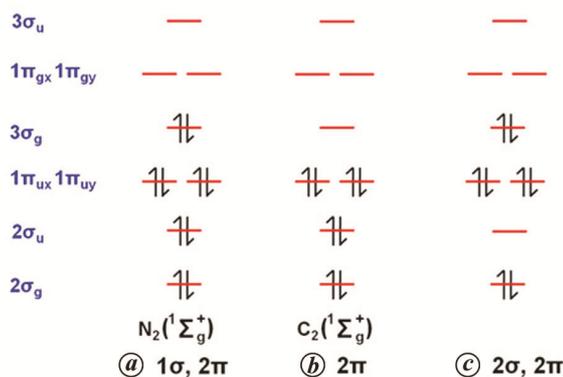


Figure 2. *a*, Electronic configuration of N₂; *b*, Dominant configuration 70.9% of the ground state of C₂; *c*, The excited state configuration that contributes 13.6% to the ground state of C₂.

decrease of bond order can be monitored with each excited state. The ground state singlet Σ_g^+ has 70.9% contribution from a configuration with a formal double bond, both π (Figure 2 b) and 13.6% from a configuration with a quadruple bond, 2π bonds and 2σ bonds (Figure 2 c). The three excited state PECs ($^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$) are shown to have minima corresponding to structures with three, two and one bond. The study finds that only in the nonet state ($^9\Sigma_g^+$) the PEC shows no minimum, indicating that all the four bonds are broken.

The experimental and theoretical studies reported in these recent articles bring up further questions. The precise electronic state of the C_2 obtained in the current experiment as well as those generated at high temperatures previously, have to be established. It is also necessary to generate and characterize the three excited states ($^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$) predicted here and also verify the dissociative PEC for the nonet ($^9\Sigma_g^+$). What are the associated separated carbon atom's electronic configurations? The computational results also elicit methods to assign the magnitude of σ and π bond strengths in these different electronic states of C_2 . If the contribution of the configuration with the quadruple bond (Figure 2 c) is only 1% instead of 13.6%, can one still call the ground state as quadruple bond? How and where does one draw the line? It is tempting to spe-

culate the σ and π bond energies from the dissociation energies. Assuming that strength of non-conjugated π bonds do not vary considerably, an approximate value of 64.0 kcal/mol can be obtained for a π bond from experimental data on ethylene and acetylene. The ground state of C_2 with a quadruple bond has a dissociation energy of 143.2 kcal/mol. This leaves a contribution of 15.2 kcal/mol ($143.2 - 64 \times 2$) from the two σ bonds. It appears that the weak σ bonds have only helped the C–C distance to be short at 1.24 Å; obviously it is a π bond's world. Would π bonds be shorter if there is no σ bond at all?¹³ The first excited state of the C_2 ($^3\Sigma_u^+$) formally has one σ and two π bonds, but a dissociation energy of only 116.0 kcal/mol. This leaves an estimate of negative (albeit small in magnitude) contribution ($116 - 64 \times 2$) to the dissociation energy by the lone σ bond. The absence of σ bond appears to decrease the C–C distance to 1.20 Å, 0.04 Å shorter than the ground state, supporting the tendency of π -bonds to be short in the absence of σ bond. It is clear that simple homonuclear diatomics have very complex reactivity and electronic structures⁵ and MO theory is up to the game as these authors have demonstrated convincingly⁸.

1. Pan, W. and Shevlin, P. B., *J. Am. Chem. Soc.*, 1996, **118**(41), 10004–10005.

2. Skell, P. and Harris, R., *J. Am. Chem. Soc.*, 1966, **88**(24), 5933–5934.
3. Skell, P. S., Havel, J. J. and McGlinchey, M. J., *Acc. Chem. Res.*, 1973, **6**(3), 97–105.
4. Skell, P. S. and Plonka, J. H., *J. Am. Chem. Soc.*, 1970, **92**(19), 5620–5624.
5. Miyamoto, K. *et al.*, *Nature Commun.*, 2020, **11**(1), 1–7.
6. Das, A. and Arunan, E., *J. Chem. Sci.*, 2019, **131**(12), 120.
7. Shaik, S., Danovich, D., Braida, B. and Hiberty, P. C., *Chem. – A Europ. J.*, 2016, **22**(12), 4116–4128.
8. Bhattacharjee, I., Ghosh, D. and Paul, A., *Chem. Sci.*, 2020, **11**, 7009–7014.
9. Frenking, G. and Hermann, M., *Angew. Chem.*, 2013, **125**(23), 6036–6039.
10. Hermann, M. and Frenking, G., *Chem. – A Europ. J.*, 2016, **22**, 4100–4108.
11. Itatani, J. *et al.*, *Nature*, 2004, **432**, 867–871.
12. Zhai, C. *et al.*, *Sci. Rep.*, 2016, **6**, 23236.
13. Jemmis, E. D., Pathak, B., King, B. and Schafer III, H. F., *Chem. Commun.*, 2006, 2164–2166.

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