

'increased-valence' structures.

Linnett's computational procedures could not match those now used, but because the npso structures involve better electron charge correlation than do the Kekulé structures^{10,13}, it is likely that Linnett's conclusion concerning the npso structure for C₆H₆ will be found to be valid when modern computational procedures are employed.

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SIR—We feel it necessary to correct some misconceptions that two articles by John Maddox (*Nature* **324**, 599; 1986 and **327**, 551; 1987) on our recent work^{1,2} and that of Cooper *et al.*³ may have engendered.

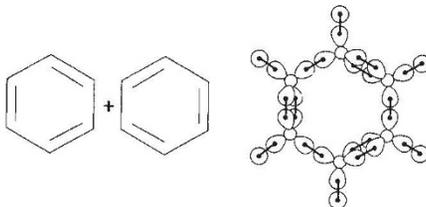
When firsts are first. The original article (about our work¹ on C₂F₂) was entitled "When firsts are really second" and took issue with the use of the word "first" to describe the results of our work. Specifically, the article suggested that our objective was to show that the "valence bond description may be a more accurate starting point for calculation of electronic structure of molecules than the molecular orbital framework" and that this conclusion had previously been made a month earlier in *Nature* by Cooper *et al.*³, refuting our claim to precedence.

What we actually had claimed was to have provided quantitative justification for the equivalent bent-bond representation (as opposed to the σ and π bond representation) of the triple bond, a description first proposed by Slater⁴ and Pauling⁵ long ago. The gross misstatement of our intent (in *Nature*) is extremely disconcerting and somewhat mystifying considering that our true objective is stated explicitly in the abstract: "These represent the first quantitative calculations which document a case where a triple 'bent-bond' description is energetically favoured over a σ, π bond description".

Bent bonds are better. The fundamental thrust of our work^{1,2} has been to address an old, but, until recently, unresolved

question: are multiple bonds in molecules better represented in terms of σ and π bonds or in terms of Ω bonds (equivalent multiple bent bonds)? Within valence bond theory (which is a higher level of theory than that of molecular orbitals), this question can be addressed. (The two descriptions are energetically indistinguishable in molecular orbital theory.)

Our work on C₂F₂ demonstrated that triple bonds are energetically better represented in terms of Ω bonds. Earlier work had established the Ω bond description for double bonds^{6,7} and later work proved this also to be the case for the canonical



σ, π system, benzene². Based on the variational principle (energetic criterion), we found that the benzene molecule was best represented in terms of two Kekulé structures where each structure was described in terms of alternating single and equivalent bent double bonds about the ring as shown in the figure. These calculations for a series of molecules represent the first quantitative evidence of the superiority of the Ω bond description, which has caused a reexamination of the conventional views of bonding. In their calculations on benzene, Cooper *et al.*³ do not even mention this most fundamental point.

When firsts are really second. The main theme of the second article was the desirability of adequate citation of complementary work. We are in full agreement that it is proper to cite work that serves as a foundation to one's own contribution. We believe, however, that the conclusion erroneously attributed to us (see first point above), and seemingly discovered by Cooper *et al.*³ is obvious and certainly predates both publications. It should be pointed out that calculations using the valence bond approach date from 1927, with the calculation of Heitler and London on the H₂ molecule⁸, and that valence bond theory was given its most powerful articulation by Pauling⁹.

Our own calculations are based on a theory first given formal expression by Hurley *et al.*¹⁰ and eventually implemented as a special case of the generalized valence bond theory¹¹⁻¹³. It would be futile to attempt to catalogue all the valence bond calculations carried out since then. Nor are calculations on benzene novel. A mention of the calculation of Cooper *et al.*³ would have added little to our discussion. An *ab initio* valence bond calculation on benzene was reported in 1973 (ref. 14), a self consistent version in 1974 (ref.

15). Indeed, Pauling has noted¹⁶ that he had predicted the results of Cooper *et al.* in 1933. The high quality configuration interaction calculations of Hay and Shavitt¹⁷ and the localized molecular orbital study of Newton and Switkes¹⁸ were pertinent to our discussion as they question the σ, π orbital description.

Prudence. Hay and Shavitt¹⁷ reported a self consistent field (SCF) energy of -230.6410 hartree. Using the same gaussian basis set (with a minor difference in the contraction), Cooper *et al.*³ calculate an SCF energy -229.9954, which is more than 17 eV higher. Our calculation², again with the same basis set but this time with the same contraction as Cooper *et al.* finds an SCF energy of -230.6404, in agreement with Hay and Shavitt¹⁷. The magnitude of the discrepancy, 17.6 eV, points to only one conclusion: the calculation of Cooper *et al.* is flawed.

As the SCF value had been published over ten years earlier, the lapse in responsibility of the authors to examine the literature and the failure of the system of review to catch this oversight can only serve as an embarrassment to both authors and editor. Thus we believe your critical comments to be without foundation and take exception to them. The interested reader should also note the article in *New Scientist* **115**, 30 (1987).

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SIR—John Maddox (*Nature* **327**, 551; 1987) has discussed two calculations of the electronic structure of the benzene