Tetrahedron. 1962, Vol 17, pp 229 to 233. Pergamon Press Ltd. Printed in Northern Ireland

THE CARBON-CARBON TRIPLE BOND AND THE NITROGEN-NITROGEN TRIPLE BOND*

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Abstract—The unshared-pair orbital of a nitrogen atom in :N. N: is estimated to have 21 per cent *p* character and 79 per cent *s* character. The nature of this orbital is such that the energy of repulsion between unshared pairs for the nitrogen nitrogen triple bond is expected to be very small, whereas it is large, about 40 kcal/mole, for N--N and N N; in consequence the triple bond is especially stable. For—C C--, on the other hand, there is significant repulsion energy of the electrons involved in the adjacent single bonds, causing instability of the triple bond.

THE carbon-carbon triple bond may be described as involving three bent bonds, with the bond orbitals for the three bent bonds as well as the fourth (outer) bond approximately tetrahedral orbitals, with 25 per cent *s* character, about 44 per cent *p* character, 4 per cent *d* character, and 2 per cent *f* character.[1] This description and also the corresponding description of the carbon-carbon double bond are compatible with the observed values of bond lengths and bond angles and of some other properties of substances containing these bonds.

There is, however, an interesting irregularity[2] in the values of the bond energy for the sequence C—C, C C, C..C in comparison with the sequence N—N, N N, N N. An explanation of the irregularity is proposed in the following paragraphs.

It is seen from Fig. 1 that the C C bond and the N N bond have bond energies greater than those of the corresponding single bonds by the same amount, 63 ± 1 kcal/mole. If the same difference in energy held also for the additional bond in the triple bonds, their bond energies would be 210 kcal/mole for C -C and 163 kcal/mole for N_N. The observed values are 194 kcal/mole and 226 kcal/mole, respectively; the nitrogen-nitrogen triple-bond energy is 32 kcal/mole less than the carbon-carbon triple-bond energy, rather than 47 kcal/mole greater, as might be expected from the values for the double bonds and single bonds. The anomaly to be accounted for is thus 79 kcal/mole.

This anomaly is related to an anomaly in sequences of values of single-bond energies that has been discussed by Pitzer[3]. For C- C, Si—Si, Ge -Ge, Sn -Sn the values of the single-bond energies, 83, 42, 38, and 34 kcal/mole, respectively, decrease in a reasonable way with increase in period number. For each of the other sequences the value for the first-row element is very small, smaller than for its second-row congener: 38, 51, 32, 30 for N--N, P -P, As—As, Sb- Sb; 33, 51, 44, 33 for O O, S—S, Se—Se, Te—Te; and 37, 58, 46, 36 for F- F, Cl—Cl, Br—Br, I -I. Pitzer pointed out that the difference between C—C on the one hand and N—N, O—O, and F F on the other is that the atoms N, O, and F have one or more unshared electron pairs, whereas carbon has only shared electron pairs in its valence shell, and that the

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* Contribution No. 2677 of the Gates and Crellin Laboratories of Chemistry.

[1] L. Pauling, *Proc. Nat. Acad. Sci. U.S.* **44**, 211 (1958); *Theoretical Organic Chemistry, Kekulé Symposium* pp. 1-7. Butterworths, London (1958).

[2] L. Pauling, *The Nature of the Chemical Bond* (3rd Ed.) p. 191. Cornell University Press, New York (1960).

[3] K. S. Pitzer, *J. Amer. Chem. Soc.* **70**, 2140 (1948).

repulsion of the unshared pairs causes the bond energy to be abnormally small for N - N, O - O, and F - F. He attributed the absence of a similar strong repulsion of unshared pairs in P- P, etc., to large values of the interatomic distance caused by repulsion of inner shells. Pitzer did not discuss the triple-bond anomaly described above.

This anomaly cannot be attributed to a difference in the bond orbitals of the bent bonds that constitute the triple bonds. It is true that the orbitals are somewhat different: for carbon they are tetrahedral bond orbitals and for nitrogen they are *p* orbitals with only a small amount of *s* character, about 7 per cent as estimated by a rough calculation[4] and detailed quantum-mechanical treatments.[5] (The *d* character and *f* character are ignored in the following discussion, which would not be changed much by their inclusion.) The maximum strength of this *sp* hybrid bond orbital for nitrogen, 1·93, is a little less than that of the sp^3 tetrahedral orbital for carbon, 2·00, and the nodal angle, 99°, is also less than the tetrahedral angle, 109·5°. These differences should not affect the bond energy greatly, and in particular should not affect the triple bond in a strikingly different way from the double bond.

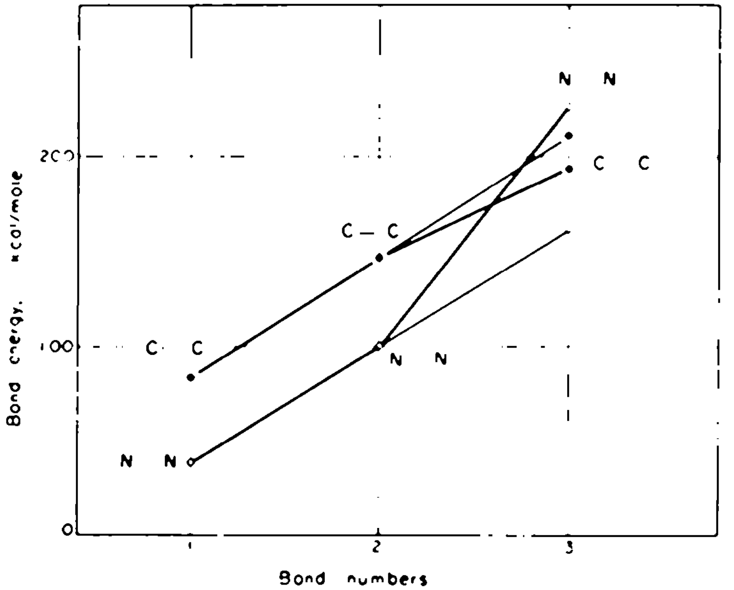

FIG. 1. Experimental values of bond energies for single, double, and triple bonds between carbon atoms and between nitrogen atoms. For triple bonds the values obtained by linear extrapolation from the single-bond and double-bond values are also shown.

There is, however, a significant difference in nature between acetylene and the nitrogen molecule: the fourth orbital of each of the carbon atoms in acetylene is a bond orbital, used in the C—H bond, whereas the fourth orbital of each nitrogen atom in N_2 is occupied by an unshared pair of electrons, and this fourth orbital differs greatly from the bond orbitals in such a way as to affect the N—N and N=N bonds differently from the N≡N bond.

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[4] Ref. 2, p. 120.

[5] R. S. Mulliken, *J. Phys. Chem.* 56, 295 (1952); C. W. Scherr, *J. Chem. Phys.* 23, 569 (1955).

The unshared-pair orbital accompanying three *s*-*p* bond orbitals with 7 per cent *s* character has 79 per cent *s* character and 21 per cent *p* character. It has no nodal cone (which appears first at 25 per cent *p* character), but has a very small value at 180° from the direction of its maximum (Fig. 2).

Let us consider the interactions of the electrons of two atoms A and B that are not involved in the A—B bond. For ethane, for example, these are the three electrons of carbon atom A that are involved in the C—H bonds to the three hydrogen atoms attached to atom A and the three corresponding electrons for the other carbon atom B. Each of the three electrons of atom A interacts with each of the three electrons of atom B in such a way as to introduce an exchange integral into the energy expression with the coefficient −1/2 (in place of +1 for two electrons involved in the formation of a shared-electron-pair bond).

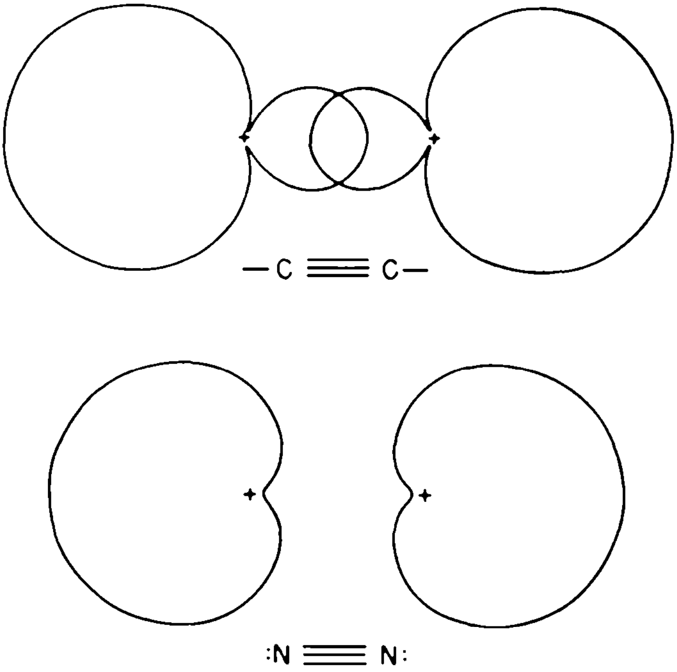

FIG. 2. The upper part of the diagram shows the angular dependence of tetrahedral bond orbitals for the single bonds of two carbon atoms connected by a triple bond. The large lobes extending outwards are involved in overlap with the hydrogen-atom orbitals in acetylene. The small lobes, extending inwards, overlap to produce repulsion, decreasing the energy of the carbon–carbon triple bond. The lower part of the diagram shows the angular distribution for the nitrogen orbitals occupied by unshared pairs in the nitrogen molecule. These orbitals are assumed to have 21 per cent *p* character. The angular distribution is such that there is little repulsion between the two unshared pairs in the nitrogen molecule, but large repulsion between these pairs in molecules in which two nitrogen atoms are connected by a double bond or a single bond.

These interaction terms are not large, although they are presumably large enough to produce the potential maxima of about 3 kcal/mole restricting rotation about the C—C bond.[1] Their magnitude may be estimated from the strength of the two orbitals concerned along the bond direction. For a tetrahedral orbital the nodal angle is the tetrahedral angle, and hence the strength of the orbital is zero in this direction, and the exchange integral and the interaction energy are expected to be small. For ethylene, too, the direction of the double bond lies close to the nodal cone for the two carbon orbitals involved in C—H bonds and the strength of these orbitals in the double-bond direction (122° from the C—H direction) is small, so that the interaction energy of these electrons should not change the energy of the C=C bond very much.

In acetylene, however, the two carbon orbitals involved in the C—H bonds have their rather large negative lobes pointed directly toward one another, as shown in Fig. 2, and hence their interaction should decrease the C≡C bond energy considerably.

With the exchange integral taken as roughly proportional to the product of the strengths of the orbitals along the internuclear direction, its value is seen to be ¼ of the value of the integral with overlapping of the large lobes (with $S = 2$, compared with -1 for the small lobes). With the factor $-\frac{1}{2}$ in the quantum mechanical energy expression, the interaction energy of repulsion of these electrons becomes one eighth of that corresponding to maximum overlap. For the distance 1·54 Å the exchange integral may be roughly approximated at 83 kcal/mole, the energy of the single bond. However, a larger value of the exchange integral should probably be used, corresponding to the smaller carbon–carbon distance, 1·20 Å. It is difficult to make a thoroughly reliable estimate of the factor to be used for this correction, but the relation between bond energy, bond number, and bond length for fractional bonds ($n < 1$) indicates that the factor 3 should be used.[6] This leads to 31 kcal/mole for the repulsion energy of the two electrons occupying the outer orbitals of the two carbon atoms in acetylene. The same calculation with orbitals with 25 per cent *s*, 69 per cent *p*, 4 per cent *d*, and 2 per cent *f* character (strength 2·76 for positive lobe, −0·86 for negative lobe) leads to 15 kcal/mole. This effect may accordingly explain the difference 16 kcal/mole between the value 194 kcal/mole for the C≡C bond energy and the value 210 kcal/mole obtained by extrapolation of C—C and C=C.

For nitrogen-nitrogen bonds the principal repulsion is that between the unshared pairs of electrons of the two nitrogen atoms, for which the exchange integral has the coefficient −2. The ratio of the square of the strength of the unshared-pair orbital (Fig. 2) in the triple-bond direction to the square of the strength of the nitrogen bond orbital is 0·0012, and the energy of repulsion of the unshared pairs in the N_2 molecule is hence calculated to be 0·5 kcal/mole. The correction is accordingly very small.

For N—N and N=N the energy of repulsion is much larger, in agreement with the argument advanced by Pitzer[3]. It is difficult to make reliable calculations because of the rapid change of orbital strength with angle and uncertainty about the angle between the orbital axis and the bond direction. A rough calculation gives about 40 kcal/mole for both N—N and N=N (including both unshared pairs and outer bond orbitals), in approximate agreement with indication from the congener sequences.

Although this simple treatment does not permit a reliable quantitative calculation to be made, it seems justified to conclude that the bond energies for N—N and N=N are low because of large repulsion-energy terms involving the unshared electron pairs, and that the relative stability of the :N≡N: triple bond is to be attributed to the smallness of the repulsion between the unshared pairs.

The suggestion made by Pitzer[3] that an increased interatomic distance caused by repulsion of inner shells is the explanation of the apparent absence of unshared-pair repulsion for P—P and similar bonds is, I think, to be rejected. For the same kinds

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[6] Ref. 2, pp. 231, 400

of hybrid bond orbital and hybrid unshared-pair orbital for phosphorus as for nitrogen, the ratio of unshared-pair repulsion energy to bond energy should be the same for P—P as for N—N. If, however, the hybrid character of the phosphorus orbitals were different from that of the nitrogen orbitals in such a way as to permit the unshared pair to swing farther away from the adjacent bonded atoms, the repulsion energy would be greatly decreased. This difference in hybrid character could involve a larger contribution of the *d* orbital for phosphorus than for nitrogen; and, indeed, a much larger contribution of 3*d* to the 3*s*3*p* hybrid orbitals for phosphorus is to be expected than of 3*d* to 2*s*2*p* for nitrogen, because of the far smaller promotion energy involved. I doubt that repulsion of inner shells is of much significance in bonds such as P—P.