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Electronic structures of the boron cage molecules B_4H_4, B_4Cl_4 and B_4F_4

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Ab initio calculations have been performed on B_4H_4, B_4Cl_4 and B_4F_4 in order to aid our understanding of the bonding in these compounds, which is presumably based on a tetrahedral boron cage. This cage has only 8 electrons and so is less than that expected on the basis of the usual framework electron counting rules. Basis sets with polarisation functions were used at the SCF, CI and CPF levels of theory to confirm that the T_d structures are indeed more stable than the D_{4h} ones. Davidson-Roby population analyses were able to show that many factors, including 3-centre 2-electron bonding and back-bonding from the ligand to the boron cage, are of importance in determining the relative stability of the three compounds, of which B_4Cl_4 is the only one that has yet been observed experimentally.

Key words: B_4H_4 — B_4Cl_4 — B_4F_4 — Stabilities — Geometries — Population analyses — Multi-centre bonding

1. Introduction

The closed deltahedral molecules B_4Cl_4 (tetrachlorotetraborane(4)) [1-4], and $(Me_3C)_4B_4$ (tetrakis (1,1-dimethylethyl) tetraborane(4)) [5], are unusual in that they are found to have only 8 electrons in the tetrahedral boron cage. According to the usual electron counting rules [6, 7], 10 valence electrons within the cage would be expected for a delocalised bonding network and 12 electrons (2 electrons for each of the 6 B-B bonds) for a localised one. Various mechanisms have been proposed to stabilise the presumably electron deficient boron cage and at the same time rationalise the non-existence of B_4H_4 and B_4F_4. The most prominent amongst these involves a back-bonding process whereby valence electrons from the ligand contribute to boron cage bonding [2, 5, 8]. Others suggest that the nature of the boron-ligand σ bonds or multi-centre boron-boron bonds are important factors [2, 8-10]. The difficulties involved in quantifying back-bonding effects have already been discussed with reference to tetrahedral cage bonding [10], nevertheless quantitative calcuations have managed to confirm such processes; Davidson's study on BF [11] is a standard example. Similarly, the idea of multi-centre bonding is not new and it has been examined within the context of the bonding in B_4Cl_4 and B_4F_4. However, it was recognised at the time that the basis sets may have been inadequate [8].

It is the aim of this paper to examine the bonding in the three compounds B_4H_4, B_4Cl_4 and B_4F_4. Our purpose was to determine the equilibrium structures within the confines of the T_d and D_{4h} point groups and analyse the differences in bonding across this series. Despite the high symmetry, previous efforts have been limited at best to SCF calculations with minimal basis sets [8-10]. We have extended these earlier calculations by performing SCF geometry optimisations with basis sets which contain polarisation functions. The influence of correlation effects has been evaluated using CI and CPF methods for B_4H_4 and B_4F_4 only, as size limitations restricted such calculations for B_4Cl_4.

The multi-centre contributions to the bonding in these compounds have been computed using a Davidson-Roby [11, 12] analysis, as a Mulliken [13] analysis does not give such effects and is also too sensitive to basis set variations. Such a thorough treatment should provide information as to which structures are stable, and by what means they are stabilised.

2. Computational methods

The basis sets employed were constructed from the Huzinaga primitive sets [14]. Two basis sets were used for each molecule, a smaller basis, denoted SB, of approximately DZ quality and a larger, denoted LB, incorporating in addition to a slightly expanded core basis, a single standard polarisation function on all atoms. In choosing our bases we hoped to accurately describe the ionic nature of the bonding and, in the case of B_4F_4, keep the basis to a size that would permit correlation calculations. Thus, we developed our LB basis for B_4F_4 from a $(10s, 6p)$ primitive set on F and a $(8s, 4p)$ primitive set on B. The basis set details are given in Table 1.

The geometries, constrained to T_d or D_{4h} symmetry, were optimised using SCF and analytic gradient programs [15]. Especially for calculations with polarised basis sets, a new direct SCF (DSCF) program was responsible for significant improvements in computational efficiency [16]. As well as taking advantage of the molecular symmetry, it estimates the time required for the evaluation of integral batches, thus restricting storage of integrals to only those which are expensive to calculate. Convergence to the equilibrium geometry was determined by the criterion that the internal coordinate gradients were less than 10^{-3} a.u. The CI and CPF calculations [17] for B_4H_4 and B_4F_4 were performed with the Karlsruhe version [18] of the Columbus system of program [19-21], at the SCF

Table 1. The basis sets for B_4H_4, B_4F_4 and B_4Cl_4

	SB	LB
B_4H_4	$(8s, 4p; 45s) \rightarrow [4s, 2p; 2s]$	$(9s, 5p, 1d; 5s, 1p) \rightarrow [5s, 3p, 1d; 3s, 1p]$
B_4F_4	$(8s, 4p; 8s, 4p) \rightarrow [4s, 2p; 4s, 2p]$	$(8s, 4p, 1d; 10s, 6p, 1d) \rightarrow$ $[4s, 2p, 1d; 5s, 3p, 1d]$
B_4Cl_4	$(8s, 4p; 11s, 7p) \rightarrow [4s, 2p; 6s, 4p]$	$(9s, 5p, 1d; 11s, 7p, 1d)$ $\rightarrow [5s, 3p, 1d; 6s, 4p, 1d]$

Polarisation exponents: $H(p=0.8)$; $B(d=0.5)$; $F(d=1.40)$; $Cl(d=0.65)$

Table 2. Energies (E_h) and SCF optimized geometries (a_0) for the T_d and D_{4h} structures of B_4H_4, calculated with the SB and LB basis sets

Basis symmetry	SB T_d	D_{4h}	LB T_d	D_{4h}
E SCF	−100.8655	−100.8151	−100.9479	−100.8735
CI	−101.1102	−100.9660	−101.3122	−101.1930
CPF	−101.1460	−100.9790	−101.3729	−101.2401
$r_{B\text{-}B}$	3.231	3.387	3.184	3.389
$r_{B\text{-}H}$	2.244	2.269	2.230	2.252

optimised geometry, and with a computational reduction in symmetry to the subgroups D_2 and D_{2h} from T_d and D_{4h} respectively. The 1s core orbitals were kept frozen in the correlation calculations, as well as one high-lying virtual MO per BX moiety. Davidson-Roby popultion analyses [11, 12] were performed to partition the charge distribution into net atomic charges and shared electron numbers (SENs) for two or multi-centre bonds [22]. All calculations were carried out on the Siemens 7881 and Cyber 205 at Karlsruhe.

3. Results and discussion

3.1. Energetics

The calculated energies and optimised geometries for B_4H_4, B_4Cl_4 and B_4F_4 are presented in Tables 2-4. With the basis set denoted by LB, which will be used

Table 3. SCF energies (E_h) and optimized geometries (a_0) for the T_d and D_{4h} structures of B_4Cl_4, calculated with the SB and LB basis sets

Basis symmetry	SB T_d	D_{4h}	LB T_d	D_{4h}
E SCF	−1936.4965	−1936.4782	−1936.6585	−1936.6199
$r_{B\text{-}B}$	3.213[a]	3.305	3.191[a]	3.334
$r_{B\text{-}Cl}$	3.340[a]	3.379	3.282[a]	3.297

[a] Experimental values [1]: $r_{B\text{-}B} = 3.23 \pm 0.08$ au; $r_{B\text{-}Cl} = 3.21 \pm 0.06$ au

Table 4. Energies (E_h) and SCF optimized geometries (a_0) for the T_d and D_{4h} structures of B_4F_4, calculated with the SB and LB basis sets

Basis	SB		LB	
symmetry	T_d	D_{4h}	T_d	D_{4h}
E SCF	−496.3977	−496.3813	−496.7551	−496.7134
CI			−497.7036	−497.6334
CPF			−497.9258	−497.8394
r_{B-B}	3.232	3.325	3.247	3.381
r_{B-F}	2.547	2.576	2.463	2.481

predominantly in the following discussions, all the T_d structures were found to be more stable than the corresponding D_{4h} ones by over 100 kJ mol^{-1} (1 au ≡ E_h = 2625.5 kJ mol^{-1}) at the SCF level. The addition of polarisation functions to the basis (from SB to LB) produces additional stabilisation of the T_d structures over the D_{4h} ones.

This stabilisation of the T_d structures is further enhanced when correlation effects are included via CI or CPF. A rationalisation for this result is that a tetrahedral structure at the SCF level is more crowded electron-wise than a square-planar D_{4h} structure, and correlation corrections alleviate this crowding. At the CPF level, stabilisation of the T_d structure over the D_{4h} one is greater for B_4H_4 (349 kJ mol^{-1}) than for B_4F_4 (227 kJ mol^{-1}). Although no calculation beyond the SCF level was performed for B_4Cl_4, we would expect the tetrahedral structure for this molecule to be similarly stabilised over the square-planar structure by correlation effects.

At the SCF level the D_{4h} structures of B_4Cl_4 and B_4F_4 have positive electron affinities, i.e. they have an unoccupied molecular orbital with a negative orbital energy. If this is in fact the case then a change to the T_d form is most likely. It is worth noting that reduction to dianions is not favoured for the T_d structures, unlike most other compounds with the general formula B_nX_n, beacuse the LUMO is a degenerate orbital of e symmetry and its occupation would distort the molecule.

All three B_4X_4 molecules (X = Cl, F, H), T_d and D_{4h}, were found to be stable with respect to dissociation into 4 BX monomers. A binding energy of ≈1100 kJ mol^{-1} was computed for B_4H_4 (T_d) at the SCF and CI levels, while stability is further increased at the CPF level by ≈200 kJ mol^{-1}. As CPF correctly accounts for size extensivity effects and CI does not, only the CPF calculations can be considered reliable when comparing BX with B_4X_4. The binding energy of B_4F_4 (T_d) was markedly lower, about 500 kJ mol^{-1} with the SCF and CPF methods. In comparison, for the only molecule of the three that has yet been prepared, B_4Cl_4 (T_d), a binding energy of ≈800 kJ mol^{-1} was calculated at the SCF level. These results suggest the possibility that B_4H_4 and B_4F_4 could also be prepared, although even in an inert matrix this would be difficult.

3.2. *Geometries*

The optimised geometries for B_4H_4, B_4Cl_4 and B_4F_4 (in Tables 2-4, resp.) are the first that have been computed for these compounds with basis sets of at least double-zeta quality. Previously, only geometries obtained from experimental measurements or determined by optimisations with minimal basis sets had been used in theoretical calculations. For unusual, e.g. tetrahedral, structures this may be inadequate if subsequent computations, e.g., population analyses, are to be performed as the calculated charge distribution may not reflect the "true" situation. The calculated SCF T_d geometry of B_4Cl_4 ($r_{B-B} = 168.9$ pm, $r_{B-Cl} = 173.7$ pm; N.B., 1 au $\equiv a_0 = 52.9177$ pm) is in good agreement with experiment ($r_{B-B} = 171 \pm$ 4 pm, $r_{B-Cl} = 170 \pm 3$ pm); most of the difference could be attributed to correlation effects, which are not included in our treatment of B_4Cl_4.

In general it was found that B-X bond distances varied according to the size of X, as would be expected. In B_4F_4 and B_4Cl_4 the B-X distances were larger than in the corresponding monomers by 0.080 a_0 and 0.028 a_0 resp., indicating a possible reduction in the back-bonding effects which are so dominant in the BF [11] and BCl monomers. The B-B distances are about the same for all three molecules but react quite differently to the addition of polarisation functions to the basis. While there is a shortening of the BB distances in B_4H_4 (by 0.047 a_0), and to a lesser extent, in B_4Cl_4 (by 0.022 a_0), as the basis is enlarged from SB to LB, the corresponding length in B_4F_4 is increased (by 0.015 a_0). These changes could be, in part, attributed to differences in the core bases but another explanation is possible. Polarisation functions generally cause a shrinkage of bond lengths, so some other factors are involved. A discussion of the electron distribution within the bonds, couched in terms of the shared electron numbers, can shed light on this problem.

3.3. *Population analyses*

Population analyses performed on the B_4X_4 compounds and their corresponding BX monomers were of two types: a Mulliken analysis and a Davidson-Roby analysis. As a Mulliken analysis shows a marked basis set dependency, the only clear trend that could be discerned was that in the B_4X_4 compounds, B_4F_4 had the most ionic B-X bonds (net charges on B are 0.22, 0.07 and 0.04 for B_4F_4, B_4Cl_4 and B_4H_4, respectively).

The output from a Davidson-Roby analysis is more enlightening and gives the SENs [22], which reflect covalent bond strengths and elicit information about explicit multi-centre effects. The SENs for the B_4X_4 compounds are given in Table 5 and those for BX in Table 6. The B_4X_4 SENs show clearly the presence of strong bonding networks, particularly for the T_d structures and noticeably so in B_4H_4 and B_4Cl_4. Strong two-centre σ bonds have typical values of SEN ≈ 1.4, while typical values of the three-centre two-electron (3c-2e) SENs are of the order of 0.01 [24] in normal-valency compounds. The large three-centre (B-B-B) contributions (0.69, 0.51 and 0.26 for B_4H_4, B_4Cl_4 and B_4F_4 resp.) give credence to the notion that bonding in the tetrahedral boron cages is stabilised by 3c-2e

Table 5. Shared electron numbers (SENs) for the T_d and D_{4h} structures of B_4H_4, B_4Cl_4 and B_4F_4, obtained at the SCF level with the LB basis

Molecule	Symmetry	SEN		
		B-B	B-B-B	B-X
B_4H_4	D_{4h}	2.00, 0.92[a]	0.41	1.40
	T_d	1.87	0.69	1.46
B_4Cl_4	D_{4h}	1.63, 0.54[a]	0.34	1.61
	T_d	1.60	0.51	1.44
B_4F_4	D_{4h}	1.61, 0.59[a]	0.41	1.49
	T_d	1.37	0.26	1.39

[a] The first number refers to B-B neighbours, the second to B atoms diagonally opposed to one antoher

bonding, essentially extending over each face of the tetrahedron. Such a picture is similar to the bonding in B_2H_6 (SEN(BHB) = 0.7), where 3c-2e contributions dominate, and also in P_4 (SEN(PPP) = 0.25) [24].

The extent of the three-centre B-B-B bonding is demonstrated more clearly if a Boys' localisation [25] is performed on the 8 bonding MOs of B_4H_4. Two sets of four equivalent Localised Molecular Orbitals (LMOs) are produced — one describing B-H bonding and the other B-B-B bonding. Figure 1a is a plot of one of the LMOs in the plane of three boron atoms and Fig. 1b is of the same LMO 0.5 a_0 above (external to the tetrahedron) the B-B-B plane. Both plots are typical for 3c-2e bonding. The electron density is actually found to bulge out of the plane of the three boron atoms, as is obvious if the two plots are superimposed.

The SENs computed for the BX monomers may be compared with those of the BX moieties in B_4X_4. In the monomers SEN(B-X) increases across the series BH, BCl, BF (see Table 6), while this order is reversed in the B_4X_4 molecules. This observation of an apparent weakening of the B-F bond in B_4F_4 compared to that of BF, together with the bond length changes discussed in the last section, indicate a decreased level of back-bonding in the B-F bonds of B_4F_4.

Table 6. Energies (E_h), SCF optimized geometries (a_0) and shared electron numbers (SENs) for BH, BCl and BF, calculated with the LB basis

	BH	BCl	BF
E SCF	−25.127211	−484.089113	−124.138953
E CI	−25.214071		−124.413279
E CPF	−25.217561		−124.433544
$r_{B\text{-}X}$	2.310	3.254	2.383
SEN (B-X)	1.40	1.81 ($p_\pi = 0.66$)	2.00($p_\pi = 0.75$)
$r_{B\text{-}X}$ [a]	2.3289	3.2426	2.3860

[a] Experimental values [23]

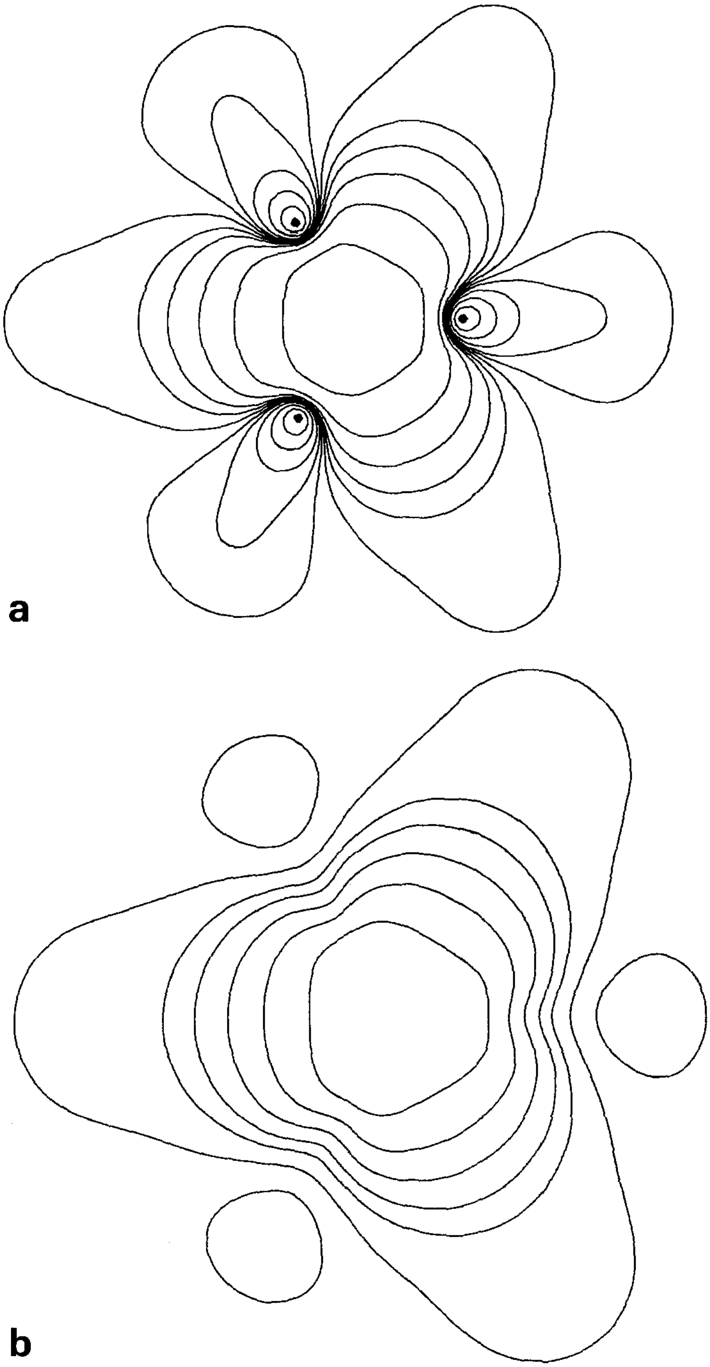

Fig. 1. Localised molecular orbital (LMO) for B_4H_4 (T_d symmetry, SCF calculation, LB basis) plotted (**a**) in the plane defined by 3 boron atoms and (**b**) 0.05 a_0 above (external to the tetrahedron) the plane in (a)

It is instructive to decompose the contributions to the B-B and B-X SENs into those arising from the valence MOs of B_4H_4, B_4Cl_4 and B_4F_4. This decomposition is given in Table 7. The major difference in the bonding of the three compounds is that the partly antibonding e, t_1 and t_2 HOMOs of B_4Cl_4 and B_4F_4, which arise from the valence p^{π} AOs (relative to the B-X bond) of Cl, F and B, are not occupied in B_4H_4 because of the absence of p electrons on H. The unoccupied t_2 orbital in B_4H_4 (from the p^{π} AOs on B) can thus stabilise the occupied t_2 orbitals (from the B-H bonds) through the coupling which is allowed through symmetry. Such a stabilisation is weaker in B_4Cl_4 and B_4F_4 since the p_{π} AOs on B are partly occupied, through back-bonding from the ligand, and so the occupied t_2 orbitals contribute less to the two-centre SENs.

The differences between B_4Cl_4 and B_4F_4 are much more complex. There is competition between two mechanisms: the electron withdrawing ability of the ligand through the σ network, which will be greater for F than for Cl; and the ability of the ligand to supply charge to the vacant p orbitals on B (back-bonding mechanism). On comparing the BF and BCl monomers it is found that both effects are greater in BF (see Table 6, $p_{\pi} = 0.75$ and 0.66 for BF and BCl, resp.). However, in the tetramers, back-bonding is reduced with respect to the monomers as the B p orbitals are also engaged in cage bonding. As a consequence, the net atomic charge in our Davidson-Roby analysis [22] is just slightly more positive on B in B_4F_4 than in B_4Cl_4 or B_4H_4 (0.07, −0.03 and 0.02, resp.). This reduced back-bonding is further highlighted if comparisons of the net atomic charges are made with the monomers (−0.21, −0.16 and 0.02 for BF, BCl and BH, resp.). Although it is difficult from the above to draw definitive conclusions it would appear that B_4H_4 and B_4F_4 constitute the extreme cases and B_4Cl_4 lies somewhere in between, probably closer to B_4F_4.

Let us now consider the construction of B_4X_4 from four BX molecules being brought in from infinity and the resulting orbital configuration (a_1 and t_2) arising

Table 7. Orbital energies (ε) and contributions to B-B and B-X SENs from the valence orbitals of B_4H_4, B_4Cl_4 and B_4F_4 (T_d symmetry), obtained at the SCF level with the LB basis set

Orbital	B_4H_4			B_4Cl_4			B_4F_4		
	ε	B-B	B-H	ε	B-B	B-Cl	ε	B-B	B-F
t_2				−0.408	0.092	−0.365	−0.442	0.096	−0.263
t_1				−0.498	−0.073	0.072	−0.706	−0.077	0.085
e				−0.514	−0.036	0.133	−0.715	−0.018	0.116
t_2	−0.399	0.227	0.064	−0.542	0.217	0.365	−0.724	0.121	0.271
a_1	−0.582	0.004	0.350	−0.618	0.031	0.155	−0.790	0.053	0.098
t_2	−0.618	0.338	0.993	−0.649	0.181	0.426	−0.806	−0.039	0.296
a_1	−0.939	1.238	0.039	−0.970	0.996	0.008	−0.966	1.145	0.017
t_2				−1.136	0.008	0.438	−1.646	−0.037	0.531
a_1				−1.145	0.136	0.189	−1.647	0.074	0.225
Total (all orbitals)		1.87	1.46		1.60	1.44		1.37	1.39

from the overlap of orbitals in the centre of the tetrahedron being formed. Implicit then in our calculations is the ability of these orbitals to rearrange so as to alleviate the increasing repulsive forces. In B_4H_4, where no back-bonding occurs, these orbitals are free to admix with the p_π orbitals on B (t_2 symmetry) and thus move to the faces of the tetrahedron. In contrast, movement of the corresponding orbitals in B_4F_4 and B_4Cl_4 is hindered by the back-bonding from the ligands, even though it is less than in BF and BCl. It appears as if a compromise is required between the forces causing back-bonding effects and those forming multi-centre cage orbitals.

The results given here are generally in agreement with the previous theoretical calculations that have been performed [8-10]. Although the basis sets used here and the level of theory could be improved, the qualitative picture is unlikely to change. Davidson-Roby population analyses are known to be relatively insenstive to the nature of the basis set, however, test calculations (see also [26]) using energy-optimal, rather than standard, polarisation functions did produce small changes (reductions) in the computed SENs, particularly for the monomers, though not sufficient to affect our conclusions.

4. Summary

We have recognised some important trends displayed by the B_4X_4 molecules. An interplay of a number of mechanisms including the degree of multi-centre bonding, the extent of back-bonding from the ligands to the tetrahedral boron cage and the electron withdrawing capability of the ligand through the σ bonding network, all contribute to the stabilisation of the T_d structures over D_{4h} structures. If the compounds are ordered as follows: B_4H_4, B_4Cl_4 and B_4F_4; then this is precisely the order of decreasing stability (with respect to dissociation into BX monomers), increasing B-B bond length, and decreasing level of bonding (as given by the shared electron numbers), both within the boron cage and to the ligands. The molecule B_4Cl_4 is the only one that has been identified experimentally, but we predict that B_4H_4 should also exhibit a high degree of stability, though in the liquid phase the hydrogen ligands may not provide sufficient protection from attack to the boron cage. Our prediction of reasonable stability for B_4H_4 can be used to help rationalise the high stability of $(Me_3C)_4B_4$ which does not require any back-bonding to be stable and for which the boron cage is protected by the four *t*-butyl groups. The results presented here are the most extensive yet performed on these molecules and have served to highlight the complexity of bonding in such systems; certainly the stability of molecules like B_4Cl_4 cannot be attributed wholly to mechanisms such as back-bonding.

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