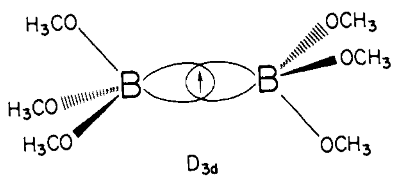

Figure 3. A D_{3d} structure for the dimer radical anion of trimethyl borate.

C_3 axis of each $B(OMe)_3$ unit is 15.7°.[13] This result may be compared with the optimum value of 10° predicted by theoretical calculations[2d] for the corresponding out-of-plane angle in the $^2A_{1g}$ ground state of $C_2H_6^+$. We conclude that, just as predicted for $C_2H_6^+$,[2] the unpaired electron in the dimer radical anion of trimethyl borate is largely concentrated in the σ-bonding orbital between two nonplanar $B(OMe)_3$ units, as represented in the D_{3d} structure for the species (Figure 3).

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(10) The value of $a(^{11}B) = 46.3$ G indicates that the semioccupied orbital possesses a much larger s character than would be expected in the case of a hypothetical bridged structure for the dimer; the corresponding coupling for $B_2H_6^-$ is ~8 G[4] and does not resolve the structural ambiguity.[5] On the other hand, the σ structure for the dimer radical anion of trimethyl borate suggests that the isotropic coupling constant of 46.3 G should be approximately half the value for the $B(OMe)_3^-$ species. Although the latter has not been determined, a value of 99.2 G can be estimated by assuming that the percentage 2s character in the semioccupied orbital of $B(OMe)_3^-$ is the same that in the isoelectronic radical $C(OMe)_3$, i.e., $a(^{11}B) = a(^{13}C)/A_0(^{13}C) \times A_0(^{11}B)$, where $a(^{13}C) = 152.7$ G (G. Brunton, K. U. Ingold, B. P. Roberts, A. L. J. Beckwith, and P. J. Krusic, *J. Am. Chem. Soc.*, **99**, 3177 (1977)), $A_0(^{13}C) = 1110$ G,[11] and $A_0(^{11}B) = 721$ G.[11]

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Methylene Singlet–Triplet Separation. An ab Initio Configuration Interaction Study

Sir:

The energy separation between the two lowest states ($^3B_1$ and $^1A_1$) of the CH_2 radical has been thoroughly investigated both experimentally and theoretically. For a review up until 1974 we refer to a paper by Harrison.[1] Still the results are in conflict. While the most accurate theoretical calculations yield values between 9 and 14 kcal/mol for the energy separation, a recent spectroscopic measurement, based on photodetachment from CH_2^-, gives the value 19.5 ± 0.7 kcal/mol.[2]

The singlet–triplet separation has recently been studied by Meadows and Schaefer on the Hartree–Fock level.[3] Very large basis sets were used and the results can therefore be expected to be close to the Hartree–Fock limit. For the $^1A_1$ state they present results both from a one-configuration ($1a_1^2\,2a_1^2\,3a_1^2\,1b_2^2$) and a two-configuration (including also $1a_1^2\,2a_1^2\,1b_1^2\,1b_2^2$) treatment, which thus includes the effect of near degeneracy between the two lowest $^1A_1$ states. The adiabatic energy differences computed with these two wave functions are 24.8 and 10.9 kcal/mol, respectively. When the near-degeneracy effect has been accounted for, the primary remaining approximation is the neglect of the dynamical correlation for the electronic motion. Another effect, which was not accounted for by Meadows and Schaefer, is the contribution due to differences in zero-point vibrational energy between the two states.

To study these effects we have performed a series of CI[15] calculations around the equilibrium geometries of the two lowest electronic states of CH_2. The direct CI method as developed in the program system MOLECULE was used.[4] For the $^3B_1$ state UHF-CI calculations were performed, i.e., the reference state is an UHF determinant and the CI expansion includes all singly and doubly replaced determinants, however, without replacing the carbon 1s orbital. For the $^1A_1$ state MC-SCF calculations[5a] were first made with a wave function comprising the two above-mentioned $^1A_1$ configurations. Using the MC-SCF orbitals as the one-particle basis set, CI calculations were then performed with all singly and doubly replaced configurations with respect to the two reference configurations. Again the carbon 1s shell was left uncorrelated. These calculations were made with a new computer program in which the direct CI method has been extended to cover also the case of a multiconfigurational root function.[5b]

A contracted Gaussian basis set was used with the primitive set[6,7] (C/11, 7, 2), (H/6, 2) contracted to ⟨C/6, 4, 2⟩, and ⟨H/4, 2⟩. The orbital exponents of the two most diffuse carbon 2p orbitals and the carbon 3d and the hydrogen 2p orbitals were optimized—using direct energy minimization techniques—on the UHF level ($^3B_1$) and MC-SCF level ($^1A_1$), respectively. The overall effect of the exponent optimization was somewhat disappointing, with only a small energy gain on the CI level. Actually the CI energies reported by Lucchese and Schaefer,[8] with a somewhat smaller Gaussian basis set—they used only one p function on hydrogen—are lower than the corresponding values with our optimized basis set. There are several reasons for this rather strange result. First, optimization of the carbon 2p and the hydrogen 2p orbitals have a neglibible effect on the energy. This probably also means that the second p function on hydrogen is rather unimportant. Second, it seems to be necessary to optimize the carbon 3d orbital, which is much more energy sensitive, on the CI level. The optimal exponents on the SCF level actually gave less correlation energy than the original guessed exponents. However, the reason for performing the exponent optimization was not primarily to obtain the lowest possible energy, but rather to get an idea of the sensitivity of the $^3B_1$–$^1A_1$ separation energy to the basis set. Since the net result of the optimization is only a change of 0.3 kcal/mol for the excitation energy, it is not likely that there are any serious defects in the one-particle basis set. The adequacy of the basis set is also borne out by a comparison with the Hartree–Fock limit calculations by Meadows and Schaefer.[3] The energies obtained here for the $^1A_1$ state are for both the one- and the two-configuration calculations, only 1.8

Table I. Calculated Properties for the CH_2 Radical

$^3B_1$	
UHF energy	−38.937655 au
CI energy	−39.060744 au
r_e	1.083 (1.08)[a] Å
θ_e	132.3° (134°)[a]
zero-point energy (E_{zp})	10.9 kcal/mol
$^1A_1$	
SCF (one configuration) energy	−38.892414 au
MC-SCF (two configurations) energy	−38.914617 au
CI_1 (2758 configurations)	−39.038789 au
CI_2 (5240 configurations)	−39.043427 au
r_e	1.112 (1.11)[a] Å
θ_e	101.4° (102.4°)[a]
zero-point energy	10.5 kcal/mol
Energy separation ($^1A_1$–$^3B_1$)	
SCF	28.4 (24.8)[b] kcal/mol
MC-SCF	14.5 (10.9)[b] kcal/mol
CI_1	13.8 (13.5) kcal/mol[c]
CI_2	10.9 kcal/mol
With ΔE_{zp}	10.5 kcal/mol

[a] Experimental values are given within parenthesis; see ref 8 for further references. [b] Near Hartree–Fock values reported by Meadows and Schaefer[3] using the RHF approximation for the $^3B_1$ state. [c] Result from work by Lucchese and Schaefer.[8]

kcal/mol higher than their corresponding energies (cf. Table I). The corresponding comparisons cannot be made for the $^3B_1$ state since it was treated in the UHF approximation in the present work. Actually this energy is 1.8 kcal/mol lower than the RHF near-limit value. For both states the bond distance and the bond angle was optimized, leading to the equilibrium structure given in Table I. These values are almost identical with the geometry used by Lucchese and Schaefer and are very close to the experimental data referred to by them.

The UHF-CI energy for the $^3B_1$ state obtained here is 0.9 kcal/mol higher than the results given by Lucchese and Schaefer. Apart from the basis set aspects of this value discussed above, we note that the effect of spin polarization, neglected in the RHF approximation, is recovered by the CI calculation, mainly through the single excitations.

For the $^1A_1$ state we performed, apart from the MC-CI calculation (CI_2 in Table I), also a single reference state CI calculation—including all single and double replacements with respect to the $^1A_1$ SCF configuration ($1a_1^2\,2a_1^2\,3a_1^2\,1b_2^2$ (CI_1 in Table I). The energy obtained for this wave function is 1.2 kcal/mol higher than the corresponding value by Lucchese and Schaefer. On this level of approximation we obtain an excitation energy of 13.8 kcal/mol, which consequently is 0.3 kcal/mol larger than the Lucchese-Schaefer value. Thus, the difference in basis set is found to have almost no effect on the energy separation.

Since the two most important configurations of the $^1A_1$ state are near degenerate, we expect a much bigger contribution from higher than double excitations for this state than for the $^3B_1$ state, where there is only one leading configuration. The CI_1 value of 13.8 kcal/mol is therefore most certainly a too large value for the separation. In the CI_2 calculation, where the reference space contains two configurations for the $^1A_1$ state we obtain a lowering of the energy by 2.9 kcal/mol. This decreases the $^1A_1$–$^3B_1$ energy difference to 10.9 kcal/mol. The energy lowering of 2.9 kcal/mol should be an estimate of the total contribution of more than double replacements to the energy separation, and does contain both linked and unlinked cluster contributions.

To check the magnitude of the unlinked cluster contribution we have calculated the CEPA corrections[9] to the UHF-CI and the CI_1 results. They amount to 3.2 kcal/mol for $^3B_1$ and 4.7 kcal/mol for $^1A_1$. The contribution to the energy difference is therefore 1.5 kcal/mol. It is hard to estimate the linked cluster contribution, but it is possible that 2.9 kcal/mol slightly overestimates the total correction from multiple substitutions.

The true nonrelativistic energy for the $^3B_1$ state has been estimated by Dykstra et al.[10] to be −39.1496 ± 0.004 hartrees. They also estimate the core-core and core-valence correlation energy to be −0.0549 hartrees. From these figures we find that 79% of the valence correlation energy is obtained in the UHF-CI calculation for the $^3B_1$ state, which means an absolute error of 21.3 kcal/mol. However, if the energy separation of 19.5 kcal/mol reported by Lineberger et al.[2] is correct, the corresponding error for the $^1A_1$ state would be only 12.7 kcal/mol. This is most unlikely since it would mean that 91% of the valence correlation energy has been obtained for this state. As a comparison, a much larger basis set for H_2O reported by Meyer[11] gives 84% of the correlation energy. The 79% valence correlation energy obtained for $^3B_1$ is a much more reasonable number.

Defects in the basis set have also been discussed by Lucchese and Schaefer. They find only minor corrections due to missing s- and p-type functions on carbon and to the neglect of core-core and core-valence correlation. The value given by Lineberger et al.[2] does also include a change in vibrational energy. We have attempted to compute the zero-point energy for the two states using the valence force method.[12] This method has proved to be very reliable for this purpose in previous work, for example on the water molecule.[13] The results are given in Table I, where it can be seen that the contribution to the energy separation is only 0.4 kcal/mol. However, the calculation assumes harmonic forces for all three degrees of freedom. This is a severe approximation for the bending vibrational mode especially for the $^3B_1$ state, where the barrier to inversion is small. Taking this into consideration would probably decrease the vibrational correction further by lowering the zero-point energy for the $^3B_1$ state somewhat. The calculation yields a contribution of 1.6 kcal/mol from the bending mode, which is then an upper limit to the correction.

Finally, the correlation effect has also been discussed by Zittel and Lineberger.[14] They compared correlation contributions obtained as differences between experimental values and accurate SCF calculations, with united atom limit results. For CH_2 the $^1A_1$–$^3B_1$ splitting was consequently compared with the oxygen ^1D–^3P splitting. A similar correlation effect, 0.24 and 0.22 eV, respectively, was obtained, which could be taken as an argument for the high experimental splitting of 19.5 kcal/mol. Such a comparison is, however, very dangerous to make in this particular case, since the O(^1D) state is described by two degenerate determinants and the $CH_2(^1A_1)$ state has two nearly degenerate determinants. Zittel and Lineberger[14] have used a one determinant description of $CH_2(^1A_1)$, while a two-determinant description would have been at least equally motivated in a balanced comparison. Since the two determinant description of $^1A_1$ would drastically change the resulting correlation effect on the splitting, we find it hard to make use of the united atom result for a prediction of the CH_2 splitting.

In conclusion the present work predicts the $^1A_1$–$^3B_1$ energy difference to be 10.5 kcal/mol, including vibrational corrections. With consideration of possible errors, this value is estimated to be within 2 kcal/mol of the correct results. It therefore seems that this calculation, together with the accompanying work by Lucchese and Schaefer, rules out the possibility of an energy separation as large as 19.5 kcal/mol.

The work on CH_2 is continued with calculations on the $^1B_1$ state and also on the negative ion CH_2. These results will be presented in a forthcoming publication.

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(15) The following abbreviations are used: HF, Hartree-Fock method; UHF, unrestricted Hartree-Fock method; RHF, restricted Hartree-Fock method; MC-SCF, multiconfiguration self-consistent field method; CI, configuration interaction; CEPA, coupled electron pair approximation.

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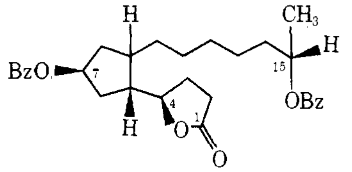
Biosynthetic Origin of the Oxygen Atoms in the C_{15} Macrolide Antibiotic Brefeldin A[1]

Sir:

Brefeldin A (**1**), a C_{15} macrolide antibiotic produced by several genera of *Ascomycetes*,[2] has an obvious structural resemblance to the prostaglandins, which has led to the speculation that **1** might also be biosynthesized from a fatty acid in a manner paralleling prostaglandin biosynthesis. Although earlier evidence obtained from labeled acetate[3,4] and malonate[4b] feeding experiments was consistent with a polyketide biosynthetic route for **1**,[5] Bu'Lock and Clay reported in 1969 that [9-^{14}C]palmitic acid apparently was specifically incorporated into **1** to a limited extent in *Penicillium cyaneum*.[6] These authors proposed a mechanism (Figure 1a) for the biosynthetic formation of the cyclopentanol ring of **1** analogous to the biosynthesis of PGG$_1$, PGE$_1$, and PGF$_{1\alpha}$ (Figure 1b). However, since the intact incorporation of palmitate into **1** could not be confirmed in *P. lilacinum* subsequently by Cross and Hendley,[7] nor in *P. brefeldianum* at Manchester,[8] this biosynthetic hypothesis was withdrawn.[7] Since the validity of biogenetic proposals like that of Bu'Lock and Clay depends on the origin of the oxygens of C-4 and C-7 of **1**—if both of these oxygens originate from the same oxygen molecule, their hypothesis could be valid mechanistically although in a slightly modified format—we sought the answer to this question via [$^{18}O_2$]acetate and $^{16,18}O_2$ feeding experiments. The results of our experiments reported herein indicate that the bioorganic parallel implicit in Figure 1 is not valid and rule out a fatty acid biosynthetic origin for **1**.

P. brefeldianum Dodge (NRRL 2083) growing in shake culture in defined media was fed sodium [$^{18}O_2$,2-^{3}H]acetate at a time when a bright yellow (unknown) pigment was just appearing. After 3 days' further incubation, labeled **1** was isolated and purified, and separate aliquots of it were converted to the 4,7-diacetate[2a] and tetrahydro-γ-lactone[2b] dibenzoate (**2**) derivatives. Using bis(4-[$^2H_3$]acetyl-7-[$^1H_3$]acetyl)-**1** and



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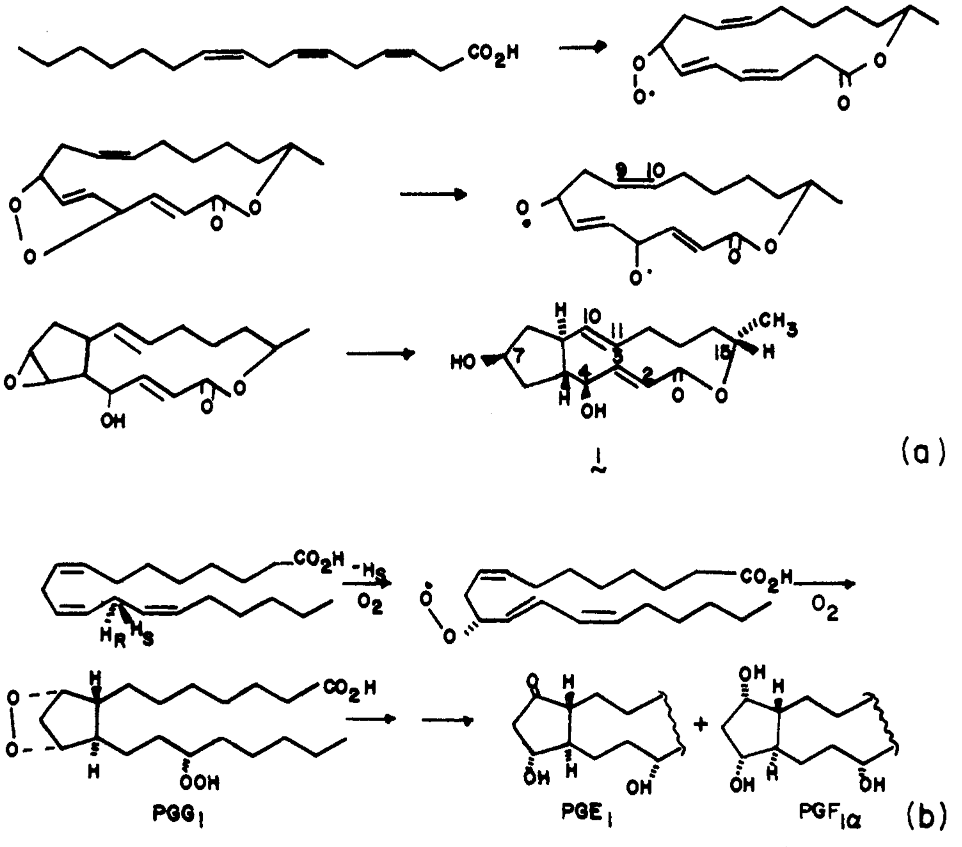

Figure 1. (a) Bu'Lock and Clay biosynthetic hypothesis for brefeldin; (b) established biosynthetic pathway of prostaglandins.