may originate similarly through the formation of adducts in which the labilities of the ligands are modified by inductive forces.

Nmr data[12] on conformational changes at cobalt also support this picture. At room temperature only one signal associated with olefinic protons is obtained (τ 5.82 for III and 6.16 for IV). The singlet splits into two equal intensity peaks at −95° for III and at −30° for IV. The coalescence phenomenon can be explained by exchange of the diene double bonds between axial and equatorial sites of the cobalt trigonal bipyramid, which can proceed, at least formally, by a pseudorotation mechanism[13] where the C=C bonds act in turn as pivots. This result, which indicates that coalescence temperatures decrease with increasingly electronegative substituents at Sn, is consistent with our hypothesis that electronegative X substituents promote the lability of the ligands at cobalt.

The syn (C_{2v}) structure of Binor-S proposed by Schrauzer and coworkers[1,2,6] is confirmed by an X-ray structure determination of the dione derivative (Figure 2), which was obtained[14] from the catalytic dimer of 7-*tert*-butoxynorbornadiene and can be converted[14] to Binor-S by Wolff–Kishner reduction. The dione, $C_{14}H_{12}O_2$, crystallizes in space group $P2_1/c$ (a = 7.914 (8), b = 12.932 (11), c = 9.614 (9) Å, β = 100° 16 (2)′, Z = 4). Intensities of 1659 reflections were measured on the Picker diffractometer (Cu Kα radiation). The structure was solved by exploiting the σ_2 relationship, and the atomic parameters, including those of the hydrogens, were refined by least squares to R = 0.049 for the 1550 reflections above background.

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[12] J. P. Heeschen, private communication. Spectra were run at 60 MHz in CD_2Cl_2 containing tetramethylsilane as internal chemical shift reference.

[13] F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

[14] T. J. Katz and R. J. Roth, private communication.

* Address correspondence to this author.

F. P. Boer*
Chemical Physics Research Laboratory
The Dow Chemical Company, Midland, Michigan 48640

J. H. Tsai
Research Department, Dow Chemical of Canada, Limited
Sarnia, Ontario, Canada

J. J. Flynn, Jr.
Eastern Research Laboratory, The Dow Chemical Company
Wayland, Massachusetts 01770

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Comments on the Barrier to Internal Rotation in Ethane

Sir:

In a recent communication,[1] an explanation of the barrier to internal rotation about the single bond in ethane was given in terms of the behavior of the two occupied pairs of orbitals of e symmetry during the rotation from the staggered to the eclipsed configuration. Since the quantitative aspects of that calculation were derived from the extended Hückel (EHMO) method,[2] we should like to point out here the implications of two accurate self-consistent-field (SCF) calculations on Lowe's explanation for the source of the barrier.

Such qualitative molecular orbital (MO) arguments as that of Lowe must rest very heavily upon symmetry and upon "all other things being equal." In the case of the ethane barrier, the latter phrase must refer at least to the equality of the bond lengths and bond angles in the two forms. The first successful MO calculation of the ethane barrier[3] employed a minimum basis set of Slater orbitals with the same bond lengths for both staggered and eclipsed ethane. As the first column of Table I shows, this calculation obtained a barrier nearly equal to the observed value and found a pattern of orbital differences almost exactly that given by Lowe's arguments. That is, the $1e_u(1e')$ orbitals gave to the barrier a small negative contribution, which was overshadowed by the much larger positive contribution of the $1e_g(1e'')$ orbitals.

In spite of their success in obtaining a good value for the barrier, Pitzer and Lipscomb[3] took care to point out the inherent limitations of this "fixed geometry" approach. It seems unreasonable to ignore the effects of possible changes in the C–C bond length and in the C–C–H angle during rotation. In fact, a simple force constant calculation[4] in which these parameters were allowed to vary gave a barrier within 10% of the experimental value, although large changes were required in the C–C distance and in the C–C–H angle upon rotation. Also, the hyperconjugation model[5] upon which Lowe's argument is based implies that the C–C bond must elongate on rotation to the eclipsed form. When we view ethane as a pseudobutadiene, we see that the C–C bond should be shorter in the trans (staggered) form than in the cis (eclipsed) configuration because of better hyperconjugation in the former.[6]

A more recent SCF calculation,[7] in which exponents and geometry were optimized for both staggered and eclipsed ethane, shows how essential the implicit hypotheses of fixed bond lengths and angles are to Lowe's conclusions. As the second column of Table I shows, in this calculation *both* pairs of e orbitals give near equal positive contributions to the barrier. Also, the $2a_1$ and $2a_2$ orbitals which Lowe dismisses as unimportant make very large positive and significant negative contributions, respectively. The optimized geometries show the increased C–C bond length and C–C–H angle predicted by the hyperconjugation argument[5] and by the force constant calculation.[4] Thus, the orbital changes discussed by Lowe[1] describe the first of two stages: (1) rotation of rigid methyl groups with C–C distance constant and (2) adjustment of the molecular geometry to the new configuration after rotation. In ethane, effect 2 tends to negate (1) as a simple explanation, but in a case where (1) is indeed dominant, an explanation like Lowe's should be useful in a qualitative sense.

Further evidence for the extremely elusive nature of the source of the ethane barrier is provided by the partitioning analysis of Table I. We see that the

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[1] J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

[2] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); **37**, 520 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[3] R. M. Pitzer and W. N. Lipscomb, *ibid.*, **39**, 1995 (1963).

[4] B. Bak, *ibid.*, **24**, 918 (1956).

[5] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[6] It is hoped that SCF calculations on *cis*- and *trans*-butadiene now in progress in this laboratory will shed further light on this problem.

[7] R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

Table I. Energy Differences[a] ($E_{\text{eclipsed}} - E_{\text{staggered}}$) for Ethane SCF Calculations

	Pitzer and Lipscomb[b]	Stevens[c]
	Energy Components	
Kinetic	0.02014	0.00994
Nuclear repulsion	0.00749	−0.11848
Nuclear attraction	−0.04898	0.20113
Electron repulsion (2-electron)	0.02657	−0.08736
	Canonical MO's[d]	
$1a_{2u}(1a_2'')$	0.00223	0.00187
$1a_{1g}(1a_1')$	0.00224	0.00182
$2a_{1g}(2a_1')$	0.00099	0.00413
$2a_{2u}(2a_2'')$	0.00106	−0.00137
$1e_u(1e')$	−0.00032	0.00215
$3a_{1g}(3a_1')$	0.00115	0.00218
$1e_g(1e'')$	0.00256	0.00265
	Localized MO's[e]	
CH		6(0.00736) = 0.04416
CC		0.04160
C inner shell		2(0.01898) = 0.03796
Scaling factors[f]	1.00659, 1.00643	1.00022, 1.00012
Barrier	0.00522 = 3.3 kcal/mol	0.00523 = 3.3 kcal/mol
Exptl, kcal/mol	2.875 ± 0.125[g]	
	3.030 ± 0.300[h]	
	2.928 ± 0.025[i]	

[a] Atomic units. [b] Reference 3. [c] Reference 7. [d] Symmetry notation for MO's is that of ref 3. First MO is the staggered conformation. MO in parentheses is the eclipsed conformation. The reader is reminded that the SCF total energy is not equal to the sum of the individual MO energies. [e] Values given are the electronic energy differences between localized MO's, analogous to the canonical MO eigenvalues given above. [f] Reference 8. First number refers to staggered configuration second to eclipsed. [g] K. S. Pitzer, *Discuss. Faraday Soc.*, **10**, 66 (1951). [h] D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958). [i] S. Weiss and G. E. Leroi, *ibid.*, **48**, 962 (1968).

contributions of the nuclear repulsion, nuclear attraction, and electron repulsion all have different signs in the two calculations, yet the calculated total barriers are within 10^{-5} au of one another. Both calculations show a positive kinetic energy barrier and a smaller negative potential energy barrier. However, if we scale the coordinates so that they satisfy the virial theorem,[8] even this small change in geometry reverses the situation, making kinetic energy contributions negative and potential energy terms positive. Finally, the "invariants" suggested by Fink and Allen[9] show no invariance between these two calculations.

An analysis of the Stevens wave function[7] in terms of localized orbitals[10] shows that the C–C, C–H, and C inner-shell orbitals make roughly equal contributions to the electronic part of the barrier. This result and the well-known importance of inner shells (as normally constituted) in the total energy make it unlikely that valence-electron-only calculations can give a complete explanation of the barrier.

In summary, we find marked discrepancies in the various contributions to the barrier between two very similar calculations. Even more surprising is the fact that SCF calculations employing vastly different basis sets have all produced barriers ranging only from 2.5 to 3.6 kcal/mol.[3,7,9,11–14] Thus, it seems that the only presently known near invariant in ethane barrier calculations is *the height of the barrier itself.* Further analysis is required to reveal other and more illuminating invariants, which may be useful in any "explanation" of the source of the barrier in ethane. Consideration of the overlap (exclusion principle) repulsion between filled C–H bond orbitals[15] may unveil one such invariant.

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(16) NSF Predoctoral Fellow.

* Address correspondence to this author.

Irving R. Epstein,[16] William N. Lipscomb*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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Structure of the $^3B_1$ State of Sulfur Dioxide[1]

Sir:

Recent interest in the formation[2] and lifetime[3] of the lowest triplet state of sulfur dioxide prompts us to report the physical constants of that state, determined by rotational analysis of the 3880-Å triplet ← singlet absorption band. In outline, the results of the analysis are that (i) the coupling scheme in the triplet state is close to case b, *i.e.*, the magnetic interactions produce splittings which are small compared with the rotational intervals; (ii) the rotational structure together with the identity of levels "missing" on account of the zero spin

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(1) Work supported in part by the National Research Council of Canada and in part by the National Science Foundation.

(2) A. McKenzie and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **308**, 133 (1968); S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, **49**, 1947 (1968).

(3) S. S. Collier, A. Morikawa, D. H. Slater, J. G. Calvert, G. Reinhardt, and E. Damon, *J. Amer. Chem. Soc.*, **92**, 217 (1970); R. B. Caton and A. B. F. Duncan, *ibid.*, **90**, 1945 (1968).