An ab Initio Molecular Orbital Evaluation of Lewis Acid Catalysis on Diels-Alder Reactions of Acrolein

O. F. Guner,[†] R. M. Ottenbrite,*[†] D. D. Shillady,[†] and P. V. Alston[‡]

Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284, and Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc., Kinston, North Carolina 28501

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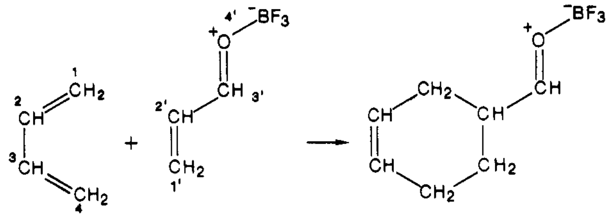
The geometries of acrolein and acrolein complexed with boron trifluoride are optimized by using STO-3G and 4-31G basis sets. The optimized geometries are utilized in STO-3G, STO-6G, STP-6G, 4-31G, and 6-31G calculations. The frontier molecular orbital energies and coefficients obtained from these ab initio calculations are used to explain the role of Lewis acid catalysis in Diels–Alder reactions. The significance of secondary orbital interactions' involvement in establishing regio- and stereoselectivity in the catalyzed reactions is supported within a minimum-basis perturbation treatment.

Diels–Alder reactions that are catalyzed with a Lewis acid are known to exhibit remarkable differences in reactivity,[1] stereoselectivity,[2] and regioselectivity[2d,3] from their thermal counterparts. Frontier molecular orbital (FMO) explanation of these effects have been reported by Houk[4] and Anh[5] and from this laboratory.[6] In these studies, the Lewis acid complex was simulated by either protonation of acrolein with the CNDO/2 method or parametrization changes with the Hückel method. We now report ab initio molecular orbital calculations of the actual Lewis acid complex between acrolein and boron trifluoride. The results of these calculations provide a clearer insight into frontier molecular orbitals of this complex and into the role of Lewis acid catalysis on the Diels–Alder reaction.[16]

Theory and Calculations

The details of FMO theory have been published.[7] The generalizations that are used to predict reactivity, stereoselectivity, and regioselectivity are as follows: (1) the pair of interacting FMO's which has the smaller energy difference makes the greater contribution to the stabilization of the transition state; (2) reactivity increases as the energy difference between interacting FMO's decreases; (3) the atoms with the larger primary coefficients (C1, C4 of diene and C1', C2' of dienophile) are bonded preferentially in the transition state; and (4) in the endo stereochemical mode of addition, the secondary orbital interactions between the inner carbon atoms (C2, C3) of the diene and the carbonyl carbon (C3') of the dienophile will be considered along with the primary interactions.[6]



The geometries of acrolein and the Lewis acid complex between acrolein and boron trifluoride were optimized with the STO-3G and 4-31G basis sets using the Schlegel gradient algorithm[8] (Table I). The total molecular energy and the energies of the frontier molecular orbitals were also obtained with STO-6G, STP-6G,[9] and 6-31G basis sets.

Results and Discussion

Calculations using the STO-3G basis set predict that the geometry of acrolein is changed only slightly upon complexation with boron trifluoride. The carbonyl double bond length is increased by only 0.01 Å, the carbon–carbon single bond length is decreased by 0.01 Å, and the carbon double bond length is unchanged within the reported significant figures (Table I). The boron–oxygen bond length is a long 1.88 Å and suggests a weak interaction between acrolein and a Lewis acid. However, the optimized geometry with a 4-31G basis set predicts a much shorter boron–oxygen distance in the acrolein–boron trifluoride complex (1.64 Å) and also larger changes in the other bond lengths of acrolein. The 4-31G basis set thus corrects the underestimated π-conjugation that is inherent in the STO-3G minimum basis and provides for an improved description of the donor–acceptor interaction between the carbonyl group and the BF_3 adduct. At the 4-31G SCF level, the energy of the complex formation is estimated to be 22.90 kcal/mol relative to geometry-optimized acrolein and boron trifluoride separately; this indicates a strong interaction with an interatomic distance only slightly larger than a normal carbon–carbon single bond. The general trends in the FMO energies and coefficients, however, are similar for calculations with both STO-3G and 4-31G optimized geometries (Table II): (1) the HOMO and LUMO energies are decreased; (2) the secondary orbital coefficient of LUMO is increased; (3) the difference between the primary coefficients of LUMO is increased; and (4) the selectivity due to the HOMO primary coefficients is reversed.

In this study the FMO energies of acrolein–boron trifluoride were also determined using several other ab initio methods that employ more gaussians than the STO-3G basis (Table III). These basis sets gave total molecular

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[†] Virginia Commonwealth University.

[‡] Du Pont.

(1) (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Inukai, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924.

(2) (a) Williamson, K. L.; Li Hsu, Y. F. *J. Am. Chem. Soc.* **1970**, *92*, 7385. (b) Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 731. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 2032. (d) Jain, P. C.; Mukerjee, Y. N.; Anand, N. *J. Am. Chem. Soc.* **1974**, *96*, 2996. (e) Baldwin, S. W.; Tomisch, J. C. *J. Org. Chem.* **1974**, *39*, 2382.

(3) (a) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3554. (b) Trost, B. M.; Ippen, J.; Vlauchick, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 8116. (c) Kakushima, M.; Espinoza, J.; Valenta, Z. *Can. J. Chem.* **1976**, *54*, 3304. (d) Tou, J. S.; Reusch, W. *J. Org. Chem.* **1980**, *45*, 5012. (e) Fringeulli, F.; Minsti, L.; Pizzo, F.; Taticchi, T.; Halls, D. J.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 1810.

(4) Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094.

(5) Anh, N. T.; Seyden-Penne, J. *Tetrahedron* **1973**, *29*, 3259.

(6) (a) Alston, P. V.; Gordon, M. D.; Ottenbrite, R. M.; Cohen, T. *J. Org. Chem.* **1983**, *48*, 5051. (b) Alston, P. V.; Ottenbrite, R. M. *J. Org. Chem.* **1975**, *40*, 1111.

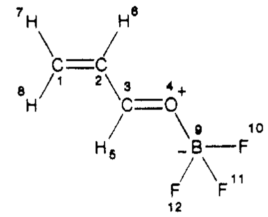
(7) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley: New York, 1976.

(8) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(9) (a) Yurtsever, E.; Shillady, D. D. *Chem. Phys. Lett.* **1976**, *40*, 447. (b) Yurtsever, E.; Shillady, D. D. *Chem. Phys. Chem. Lett.* **1976**, *43*, 20.

0022-3263/87/1952-0391$01.50/0

Table I. 4-31G and STO-3G Optimized Geometries of Acrolein and Acrolein–Boron Trifluoride

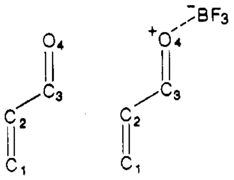


bond, Å	acrolein exptl[a]	acrolein 4-31G[b]	acrolein STO-3G	acrolein-BF$_3$ 4-31G	acrolein-BF$_3$ STO-3G
1-2	1.34	1.32	1.31	1.33	1.31
2-3	1.48	1.46	1.51	1.44	1.50
3-4	1.21	1.21	1.22	1.23	1.23
1-7	1.08	1.07	1.08	1.07	1.08
1-8	1.08	1.07	1.08	1.07	1.08
2-6	1.08	1.07	1.08	1.07	1.08
3-5	1.11	1.09	1.10	1.08	1.10
4-9				1.64	1.88
9-10				1.37	1.33
9-11				1.38	1.33
9-12				1.38	1.33

angle, deg	acrolein exptl[a]	acrolein 4-31G[b]	acrolein STO-3G	acrolein-BF$_3$ 4-31G	acrolein-BF$_3$ STO-3G
1-2-3	120.3	121.7	122.4	120.3	121.4
2-3-4	123.2	123.7	124.0	121.9	123.9
2-1-7	121.5	122.1	122.4	121.7	121.9
2-1-8	119.6	121.7	121.7	122.1	122.0
6-2-1	122.9	122.1	121.6	122.8	122.5
5-3-2	114.4	116.0	114.2	119.1	116.0
3-4-9				124.5	120.3
4-9-10				104.1	98.7
4-9-11				103.0	97.8
4-9-12				103.0	97.8

[a] From: Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1969**, *4*, 41. [b] 4-31G optimized geometry for BF$_3$; F–B–F = 120.0°, B–F = 1.33 Å.

Table II. FMO Energies and Coefficients of Acrolein and Acrolein–Boron Trifluoride



basis//geom	HOMO, eV	HOMO coefficients C1	HOMO coefficients C2	HOMO coefficients C3	HOMO coefficients O4	LUMO, eV	LUMO coefficients C1	LUMO coefficients C2	LUMO coefficients C3	LUMO coefficients O4
				Acrolein						
STO-3G//STO-3G	−9.15	−0.580	−0.535	0.231	0.422	6.11	0.643	−0.471	−0.501	0.422
STP-6G//STO-3G	−11.24	−0.570	−0.560	0.128	0.414	3.84	0.676	−0.472	−0.571	0.535
STO-3G//4-31G	−9.05	−0.579	−0.531	0.236	0.436	5.96	0.663	−0.481	−0.471	0.561
STP-6G//4-31G	−11.18	−0.566	−0.555	0.134	0.435	3.68	0.697	−0.482	−0.541	0.529
				Acrolein–Boron Trifluoride						
STO-3G//STO-3G	−10.29	0.568	0.569	−0.139	−0.402	4.49	0.610	−0.370	−0.600	0.567
STP-6G//STO-3G	−12.43	0.558	0.598	−0.033	−0.520	2.21	0.646	−0.373	−0.661	0.356
STO-3G//4-31G	−10.53	0.329	0.328	−0.109	−0.304	3.33	0.629	−0.327	−0.612	0.543
STP-6G//4-31G	−13.08	0.534	0.601	−0.006	−0.404	1.05	0.669	−0.332	−0.667	0.492

energies that were considerably lower than the molecular energy obtained with the STO-3G basis. One basis of particular interest is labeled STP-6G in Table III. For these results a minimum basis set was constructed by fitting the Slater-Transform-Preuss[9] (STP) functional form with six cartesian gaussians in a least-square sense.[10] The desire of an experimental chemist to think in terms of a minimum basis set of valence orbitals while retaining accuracy can be achieved using the STP-6G approach rather than a split-basis such as 4-31G. Using the gaussian exponents from LEMAO functions by Pople et al.,[11] the STP functional form emphasizes the long-range behavior of the valence orbitals and makes them very sensitive to chemical effects. We recently presented[12] the fitting of the STP

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(10) O-Ohata, K.; Taketa, H.; Huzinaga, S. *J. Phys. Soc. Jpn.* **1966**, *21*, 2306.

(11) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 5001.

(12) (a) Guner, O. F.; Shillady, D. D.; Ottenbrite, R. M.; Rao, B. K.; Yurtsever, E., submitted for publication in *Int. J. Quant. Chem.* (b) Yurtsever, E. *Chem. Phys. Lett.* **1979**, *63*, 318.

Table III. Molecular and FMO Energies of Acrolein and Acrolein–Boron Trifluoride

	acrolein			acrolein–boron trifluoride		
basis//geom	mol energy, au	HOMO, eV	LUMO, eV	mol energy, au	HOMO, eV	LUMO, eV
STO-3G//STO-3G	-188.3060	-9.15	6.11	-506.9825	-10.29	4.49
STO-6G//STO-3G	-190.1410	-9.42	5.71	-511.8400	-10.54	4.12
4-31G//STO-3G	-190.4777	-10.87	2.43	-513.2921	-11.96	1.06
STP-6G//STO-3G	-190.5128	-11.24	3.84	-513.4421	-12.43	2.21
6-31G//STO-3G	-190.6759	-10.90	2.33	-513.7882	-11.99	0.97
STO-3G//4-31G	-188.3037	-9.05	5.96	-506.9700	-10.53	3.33
STO-6G//4-31G	-190.1383	-9.33	5.56	-511.8257	-10.31	2.96
4-31G//4-31G	-190.4798[a]	-10.82	2.42	-513.3026[a]	-12.49	0.23
STP-6G//4-31G	-190.5118	-11.18	3.68	-513.4513	-13.08	1.05
6-31G//4-31G	-190.6777	-10.85	2.32	-513.8000	-12.51	0.15

[a] 4-31G optimized energy for BF_3 is -322.7863 au; energy of complex formation = -0.0365 au = 22.90 kcal/mol.

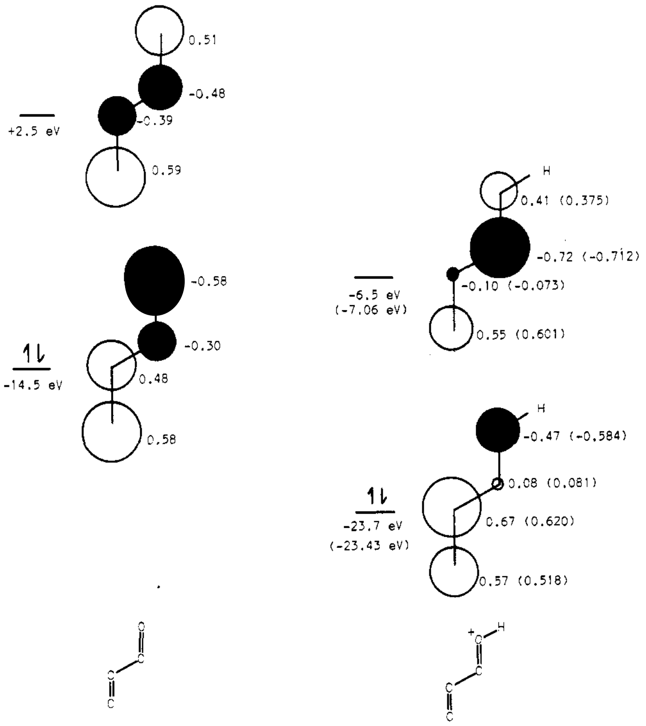

Figure 1. CNDO/2 frontier molecular orbitals of acrolein and protonated acrolein (from ref. 4). The values in parantheses are calculated by using the optimized geometry of: Dargelos, A.; Liotard, D.; Chailet, M. *Tetrahedron* **1972**, *28*, 5595.

orbital parameters to formaldehyde, ethylene, and boron monofluoride. These parameters were transfered to the present study of the acrolein–boron trifluoride complex.

Having established the accuracy of the STP-6G basis set to be comparable to LEMAO-5G results,[12] we feel confident in the use of the minimum basis concept. Of course a minimum basis such as STP-6G can not achieve the full flexibility of a split basis such as 4-31G, but the STP-6G 2p orbitals extend further than STO-6G 2p orbitals to achieve long-range sensitivity to neighboring atoms. We consider the gain in interpretability of an improved minimum basis, over that of a more flexible split-basis, to be useful. First, HOMO and LUMO one-electron energies come directly form the SCF eigenvalues. Second, the STP-6G molecular orbital coefficients are not cluttered by split-basis effects; for example in the π-orbitals, the single coefficient on each atom clearly indicates relative participation of a given atom. While this approach is customarily used in semiempirical methods, the accuracy here is better than that of an STO-6G basis set. In addition, the HOMO and LUMO molecular orbitals are simply given, and one does not need to untangle large and small components of a split-basis set. A significant additional consideration is the reduction in the size of the SCF Fock matrix using the STP-6G basis; smaller matrices mean shorter diagonalization times in the iterative SCF process. The STP-6G basis set offers several advantages for future use.

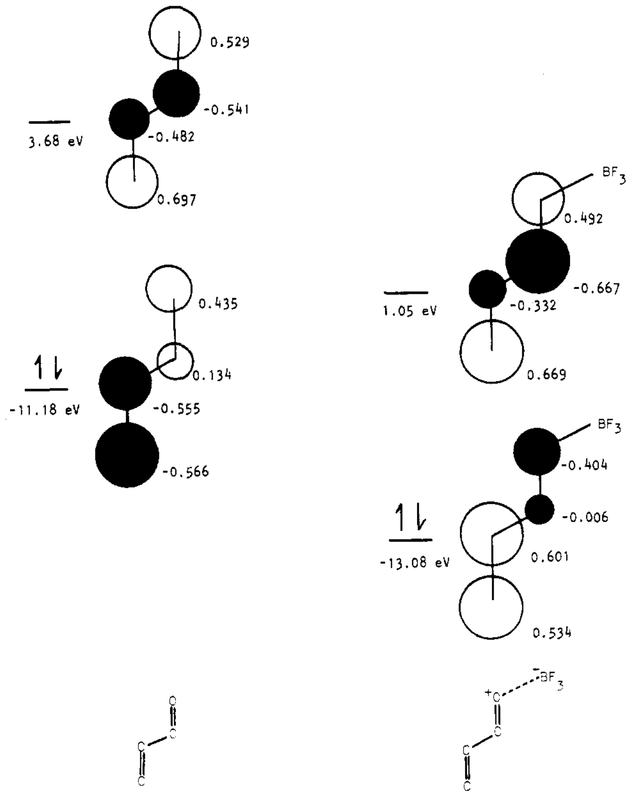

Figure 2. Ab initio frontier molecular orbitals of acrolein and acrolein–boron trifluoride complex obtained from STP-6G on the geometry optimized by 4-31G Basis.

Both the STO-3G and STP-6G calculations using the optimized geometry from 4-31G basis predicted similar decreases in the energy of LUMO (2.63 eV) and in the energy of HOMO (1.48–1.90 eV) upon complexation of acrolein with boron trifluoride (Table II). These predictions are in contrast to the much larger decreases in the energies of LUMO (9.0 eV) and HOMO (9.2 eV) that were determined for the protonated acrolein model (Figure 1). A decrease in the LUMO energy is predicted to increase the reaction rate, and the calculated decrease of 2.63 eV for the acrolein–boron trifluoride complex is only slightly larger than expected for the experimental rate increase of 10^5–10^6 times that have been reported for catalyzed reactions.[1] For example, Houk et al.[13] observed that tri-

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(13) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1970**, *98*, 937.

cyanoethylene was 10^6 times more reactive than acrylonitrile and had a LUMO energy that was lower by 2.06 eV.

The greater preference observed for the endo stereoisomer with Lewis acid catalysis can be explained from the changes in the frontier orbitals (Table II). The endo selectivity is controlled by the interaction between the carbonyl carbon (C3') of the dienophile and the inner carbons (C2, C3) of the diene. Upon complexation with the Lewis acid, the LUMO coefficient at the carbonyl carbon is increased in size (Figure 2), and thus greater stabilization can be realized from its interaction with the secondary HOMO coefficient of the diene. Additional stabilization for this interaction is obtained from the smaller energy difference between the LUMO of the dienophile and the HOMO of the diene.

In earlier studies a rationale was reported for the effect of catalysis on the regioselectivity which included both the primary and secondary orbital interactions of the FMO's.[6b] For simplicity, other investigators[4,5] have used just the primary orbital interactions which can only predict an increase in regioselectivity with catalysis while it is known that in many cases the regioselectivity is in fact decreased or reversed.[2d,3a] The ab initio FMO's in this study provide a strong theoretical justification for the inclusion of the secondary orbital interactions into the FMO approach. The difference between the primary orbital coefficients of LUMO is increased by 0.12 with both STO-3G and STP-6G basis sets, while the secondary orbital coefficient is increased by 0.14 with STO-3G and 0.13 with STP-6G. The overlap between the secondary orbitals is at a minimum 40–50% of the overlap between the primary orbitals in the transition state[14] and may be higher if nonplanarity is smaller than estimated.[15] Thus, the secondary orbital interactions are expected to have a significant effect on regioselectivity in cases where the difference between the primary orbital coefficients of the diene are small and the difference between the secondary orbital coefficients of the diene are large. Several examples of the above cases have been discussed in detail in earlier publications.[6]

It may be concluded that the ab initio calculations in this study provide further support to the important role that secondary orbital interactions play in the Lewis acid catalysis of the Diels–Alder reactions.

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Registry No. Acrolein, 107-02-8; acrolein-BF_3 complex, 105456-06-2.

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(14) Alston, P. V.; Ottenbrite, R. M.; Cohen, T. *J. Org. Chem.* **1978**, *43*, 1864.

(15) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609.

(16) While this manuscript was in press, studies of Lewis acid complexes were reported by Branchadell et al. (Branchadell, V.; Oliva, A.; Bertran, J. *J. Mol. Struct.* (*Theochem.*) **1986**, *138*, 117), who evaluated the Lewis acid catalytic effect on the Diels–Alder reactivity–selectivity relationship by means of changes in the type of energy profile from MINDO/3 calculations, and by Nelson (Nelson, D. J. *J. Org. Chem.* **1986**, *51*, 3185), who carried out a MNDO investigation to evaluate Lewis acid complexes of carbonyl compounds.

Sterically Hindered Azobenzenes: Isolation of Cis Isomers and Kinetics of Thermal Cis → Trans Isomerization

Nigel J. Bunce,* George Ferguson, Christine L. Forber, and Greg J. Stachnyk

Guelph-Waterloo Centre for Graduate Work in Chemistry (Guelph Campus), University of Guelph, Guelph, Ontario, Canada N1G 2W1

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A series of highly hindered ortho-alkylated azobenzenes has been isolated in the cis configuration for the first time. The crystal structure of one of these compounds, *cis*-2,2′,6,6′-tetraisopropylazobenzene, shows that the molecule accommodates the bulky substituents by adopting a skewed conformation and by opening up the angles of the N=N bridge (C—N=N 126.4 (2)°). This result confirms predictions that were made about the geometries of these compounds based on spectroscopic evidence and quantum calculations. The activation parameters for thermal cis → trans isomerization in this series show that there is a remarkably sharp demarcation between the existence and nonexistence of cis isomers. Provided that the cis isomer is isolable at all, it isomerizes with an activation energy of ca. 90 kJ mol^{-1}. No cases were found where the cis isomer is of only marginal stability.

We have recently reported spectroscopic and quantum mechanical studies on a series of azobenzenes substituted by alkyl groups in some or all of the ortho positions.[1] Of relevance to the present study were the cis isomers **1** to **7**. These cis compounds had electronic absorption spectra that appeared to be surprisingly insensitive to the bulk of the ortho alkyl groups. Calculations indicated that the spectra could best be explained by postulating a geometry in which the N–N–C angles of the azo bridge were opened up to ca. 125° and the phenyl rings skewed to within 30–40° of a quasi-parallel conformation. In this paper, we extend our studies of the *cis*-azobenzenes in three directions: defining the limits of steric hindrance for which a cis isomer is isolable; describing the crystal structure of the highly hindered *cis*-2,2′,6,6′-tetraisopropylazobenzene; and determining the activation parameters for the cis → trans thermal isomerization of a series of sterically hindered azobenzenes. The activation parameters were obtained in order to study the effect of ortho substitution

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(1) Forber, C. L.; Kelusky, E. C.; Bunce, N. J.; Zerner, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 5884.