of **1** and tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for **1** (24 pages); listing of observed and calculated structure factors for **1** (81 pages). Ordering information is given on any current masthead page.

Why Does Tetrafluoroethylene Not Undergo Diels–Alder Reaction with 1,3-Butadiene? An ab Initio Investigation

Stephen J. Getty and Weston Thatcher Borden*

Department of Chemistry, University of Washington
Seattle, Washington 98195

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Although the reaction of ethylene with 1,3-butadiene yields a trace of vinylcyclobutane,[1] by far the major product (99.98%) is cyclohexene, the product of a concerted Diels–Alder reaction.[2] In contrast, tetrafluoroethylene (TFE) reacts with 1,3-butadiene to give, as the only isolated product, 1,1,2,2-tetrafluoro-3-vinylcyclobutane,[3] presumably via a stepwise mechanism involving a diradical intermediate.[4] As part of an ongoing study of the effects of fluorine substituents on structure and reactivity,[5] we have investigated computationally whether the four fluorines in TFE destabilize the transition state for the Diels–Alder reaction or stabilize the transition state for diradical formation. We report the results of ab initio calculations which show that while the fluorine substituents in TFE have little effect on the relative energy of the Diels–Alder transition state, they have a profound stabilizing effect on diradical formation.

The transition state for the Diels–Alder reaction of ethylene with butadiene has previously been located by RHF calculations with both the 3-21G[6] and 6-31G*[7] basis sets. We performed RHF calculations with these two basis sets[8,9] in order to locate the transition state for the Diels–Alder addition of TFE to butadiene. The calculations described in this communication were performed with the Gaussian 86[10] and Gaussian 88[11] packages of ab initio programs.

The calculated transition-state geometry for the Diels–Alder reaction of TFE with butadiene[12] is very similar to that reported for the parent Diels–Alder reaction.[6,7] In addition, as shown in Table I, the calculated energy differences between the transition states and the reactants for the two Diels–Alder reactions are also very similar at all levels of theory. Indeed, at the RMP2/6-31G* level of theory the two energy differences are essentially the same.[13] Clearly, the presence of the fluorines in TFE has little effect on the transition state for the concerted Diels–Alder reaction of TFE.

Table I. Calculated Energies at Stationary Points on the C_2X_4 + C_4H_6 Potential Energy Surface, Optimized with the 3-21G Basis Set

	energy, hartrees		ΔE,[a,b] kcal/mol	
level of theory[c]	X = H (**4**)	X = F (**1**)	X = H (**4**)	X = F (**1**)
	Diels–Alder Transition States			
RHF/3-21G	−231.603 21[d]	−624.857 31	35.9	36.1
RHF/6-31G*	−232.879 47	−628.251 69	45.1	50.2
RHF/6-31G*[e]	−232.879 61[f]	−628.256 28	45.0	49.6
RMP2/6-31G*	−233.677 63	−629.733 17	17.0	16.8
	1,4-Diradical Intermediates[g]			
UHF/3-21G	−231.652 83	−624.947 77	4.8	−20.7
UHF/6-31G*	−232.943 58	−628.365 65	4.8	−21.3
UMP2/6-31G*	−233.650 19	−629.747 23	34.3	12.5
PUHF/3-21G	−231.667 91	−624.961 94	−4.7	−29.6
PUHF/6-31G*	−232.959 03	−628.380 09	−4.9	−30.4
PUMP2/6-31G*	−233.663 13	−629.759 39	26.1	0.4
ROHF/3-21G	−231.624 42	−624.920 69	22.6	−3.7
GVB/3-21G[h]	−231.625 27	−624.921 96	22.1	−4.5

[a] Relative to reactants (C_2X_4 + *s-trans*-1,3-butadiene). [b] Uncorrected for zero-point energies. [c] Unless otherwise stated, all energies are based on 3-21G optimized geometries (RHF or UHF). [d] Reference 6. [e] RHF/6-31G* optimized geometry. [f] Reference 7a. [g] Triplet states. [h] Singlet state.

In order to examine the effect of fluorine substituents on the transition state for diradical formation, we have performed UHF/3-21G optimizations of the all-trans conformers of the allylic 1,4-diradical intermediates in the butadiene + TFE and butadiene + ethylene reactions. Previous calculations on tetramethylene[14] and vinyltetramethylene[15] have found that these two diradicals are essentially isoenergetic with the transition states from which they are formed and that closure of these two diradicals to give cyclobutane and vinylcyclobutane, respectively, is inhibited only by small conformational barriers.

We optimized the geometries of the triplet states of the two allylic 1,4-diradicals, since closure and cleavage from the triplet states are spin forbidden. The optimized geometries for the two diradicals[12] are quite similar, with two exceptions: (i) The pyramidalization angle at the nonallylic CX_2 radical center is, as anticipated,[5] substantially larger when X = F than when X = H (ϕ = 46.6° versus ϕ = 9.6°). (ii) The new C–C bond between butadiene and TFE is shorter than the corresponding bond between butadiene and ethylene (R = 1.509 Å versus 1.555 Å). The energies of the two diradicals, relative to the reactants, have been calculated at several different levels of theory and are given in Table I. Comparison of the triplet ROHF and singlet GVB energy of each diradical shows that, as expected for trans-1,4-diradicals,[16] the two electronic states are nearly isoenergetic.

As shown in Table I, the energies of the two diradicals, relative to the reactants from which they are formed, depend on whether electron correlation is included and whether higher spin states are projected from the heavily contaminated (S^2 = 2.23) UHF wave functions of the two triplet diradicals. However, relative to the reactants, *at all levels of theory the 1,4-diradical formed from TFE is 25-26 kcal/mol more stable than the 1,4-diradical formed from ethylene*. The computational finding that fluorine substi-

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(1) Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071.

(2) For a recent review, see: Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213.

(3) Coffman, D. D.; Barrick, P. L.; Cramer, R. D.; Raasch, M. S. *J. Am. Chem. Soc.* **1949**, *71*, 490.

(4) (a) Bartlett, P. D.; Hummel, K.; Elliot, S. P.; Minns, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 2898. (b) Bartlett, P. D.; Cohen, G. M.; Elliot, K. H.; Minns, R. A.; Sharts, C. M.; Fukunaga, J. Y. *J. Am. Chem. Soc.* **1972**, *94*, 2899.

(5) (a) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (b) Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468. (c) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Phys. Org. Chem.* **1990**, *3*, 635.

(6) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

(7) (a) Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B. *J. Org. Chem.* **1989**, *54*, 2931. (b) Houk, K. N., private communication.

(8) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(9) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212.

(10) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E.; Pople, J. A., Carnegie-Mellon University.

(11) Frisch, M. J.; Head-Gorden, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA.

(12) Available as supplementary material.

(13) MP2 calculations overestimate the amount by which the correlation energy of the Diels–Alder transition state exceeds that of the reactants, but calculations at the MP4SDTQ level give an activation energy that is very close to the experimentally measured value.[7]

(14) (a) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W., Jr.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447. (b) Doubleday, C., Jr.; Page, M.; McIver, J. W., Jr. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *163*, 331. (c) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260.

(15) Bernardi, F.; Bottoni, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050.

(16) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 5409.

tution does not retard the rate of Diels–Alder addition, but accelerates the rate of diradical formation,[17] is consistent with available kinetic data.[18]

Our calculations reveal why fluorine substitution has such a profound effect on accelerating the rate of diradical formation. In the allylic 1,4-diradicals, the erstwhile π bond of the dienophile is broken and one new C–C σ bond is formed. Calculations at the (U)MP2/6-31G* level[5a,19] have found that the π bond in TFE is 18.1 kcal/mol weaker than the π bond in ethylene and that this π-bond weakening is largely due to the preference of CF_2 radical centers for pyramidal geometries. Thus, the weaker π bond in TFE is responsible for the bulk of the 25–26 kcal/mol greater relative stability calculated for the fluorinated diradical.[20] The remainder (7–8 kcal/mol) of the difference in relative stabilities must be contributed by the greater strength of the new C–C σ bond formed in the case of the TFE–butadiene addition.

Calculations show that, in general, formation of C–C σ bonds to CF_2 groups is thermodynamically more favorable than formation of such bonds to CH_2 groups. For example, replacement of one hydrogen in tetrafluoroethane by methyl is computed at the MP2/6-31G* level to be 10.0 kcal/mol more favorable than the same methyl-for-hydrogen substitution in ethane. The α fluorines contribute the bulk of this stabilization, since methyl-for-hydrogen substitution is calculated to be 8.0 kcal/mol more stabilizing in difluoroethane than in ethane when the product is 2,2-difluoropropane,[21] but only 0.8 kcal/mol more stabilizing when the product is 1,1-difluoropropane.

The greater thermodynamic stability of 2,2-difluoropropane versus the 1,1-isomer, amounting to 7.2 kcal/mol at the MP2/6-31G* level, reflects the general preference that we and others have found for the attachment of electronegative elements like fluorine[22] and oxygen,[22,23] to the more highly alkylated of two carbon centers.[24] This effect favors the formation of new C–C bonds to fluorinated carbon centers, and it contributes about 25% to the greater relative stability of the 1,4-diradical formed from reaction of butadiene with TFE, than with ethylene.

One might have expected that the weaker π bond being broken and the stronger C–C σ bond being formed would also tend to stabilize the transition state for the Diels–Alder reaction of TFE, relative to that for ethylene. These two stabilizing effects, however, are apparently offset by the destabilization, resulting from the syn pyramidalization of the two CF_2 groups that is required in this transition state. For example, we find at the RMP2/6-31G* level that syn pyramidalization of TFE to $\phi = 25.9°$ (the degree of pyramidalization found in the TFE + butadiene Diels–Alder transition state at the RHF/3-21G level) costs 4.8 kcal/mol more than does the same distortion of ethylene. By contrast, anti pyramidalization to $\phi = 25.9°$ is 0.9 kcal/mol less costly for TFE than for ethylene.

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Supplementary Material Available: Complete listing of the bond lengths and bond angles in the optimized geometries for the transition state for the Diels–Alder reaction of tetrafluoroethylene with 1,3-butadiene and for the two allylic 1,4-diradicals (9 pages). Ordering information is given on any current masthead page.

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[17] Assurance that this finding would survive MCSCF optimization of the actual transition-state geometries for diradical formation is provided by the large size of the difference between the relative energies of the diradicals and its invariance to changing levels of theory.

[18] Bartlett and Schueller have estimated that while at 175 °C 1,1-dichloro-2,2-difluoroethylene undergoes Diels–Alder cycloaddition with butadiene 50 times faster than does ethylene, this halogenated olefin undergoes [2 + 2]-cycloaddition with butadiene 10^7 times faster than does ethylene.[1]

[19] For example, we find that in the diradical formed from TFE and butadiene, planarizing the CF_2 radical center raises the energy by 11.6 kcal/mol at the UMP2/6-31G* level. This value is close to the 10.5 kcal/mol, calculated at the same level of theory, to be required to planarize the 1,1-difluoroethyl radical. Chen, Y.; Rauk, A.; Tsuchuikow-Roux, E. *J. Chem. Phys.* **1990**, *93*, 1187.

[20] This provides computational support for the suggestion, based on a thermochemical estimate of the π-bond strength in TFE, that the weakness of this π bond is largely responsible for the ease of diradical formation. Montgomery, L. K.; Schueller, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1964**, *86*, 622.

[21] The experimental value for this difference is 6.2 kcal/mol. See: Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Inc.: Deerfield Beach, FL, 1986; Vol. 3, p 141.

[22] (a) Wu, Y. D.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4557. (b) Getty, S. J.; Borden, W. T., manuscript in preparation.

[23] (a) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. (b) Dorigo, A. E.; Houk. K. N.; Cohen, T. *J. Am. Chem. Soc.* **1989**, *111*, 8976.

[24] Hyperconjugation of C–H bonds with the low-lying, antibonding C–X orbital, when X is an electronegative substituent, provides an attractive explanation of this phenomenon.[22b]

Cyclobis(paraquat-*p*-phenylene): A Novel Synthetic Receptor for Amino Acids with Electron-Rich Aromatic Moieties

Timothy T. Goodnow,[†,‡] Mark V. Reddington,[§]
J. Fraser Stoddart,[§] and Angel E. Kaifer*[,†]

Chemistry Departments, University of Miami
Coral Gables, Florida 33124
The University, Sheffield, S 3 7HF, United Kingdom

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In this communication we report the remarkable ability that cyclobis(paraquat-*p*-phenylene) $\mathbf{1}^{4+}$ exhibits to form *very stable inclusion charge-transfer complexes* with amino acids possessing electron-rich aromatic subunits. Several groups have described the formation of charge-transfer complexes between electron acceptors and amino acids with donor character, such as tryptophan, tyrosine, or phenylalanine.[1] Typically, these interactions are rather weak, with binding constants in the range 1–10 M^{-1}. In contrast, the title compound shows a much stronger affinity for the same amino acids in aqueous media, with binding constants about 2 orders of magnitude higher than those exhibited by simple acceptors. The origin of the added binding strength resides in the conformational rigidity of $\mathbf{1}^{4+}$, which has a box-like structure with a very well defined cavity lined by the two paraquat acceptor subunits.[2] This cavity is thus ideally suited to include donor aromatic rings.

Two of us (M.V.R. and J.F.S.) have recently reported the synthesis of $\mathbf{1}^{4+}$ (see structure in Scheme I) as well as its binding properties in acetonitrile with the three isomeric dimethoxybenzenes[2a] and catechol dimethyl ethers.[2b] We have also reported[3] the synthesis, solid-state structure, and electrochemical properties of a catenane based on $\mathbf{1}^{4+}$. Although many cyclophane hosts have been described in the literature, $\mathbf{1}^{4+}$ offers several novel design features such as (i) a rigid cavity in which the distance between the two paraquat subunits is ideal for inclusion of an aromatic ring, (ii) a substantial electron-acceptor character provided by the two paraquat subunits, (iii) redox properties (also provided by the paraquat groups) that may afford a mechanism to control

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[†] University of Miami, Coral Gables, FL 33124.

[‡] Current address: Baxter Healthcare Corporation, P.O. Box 520672, Miami, FL 33152.

[§] The University, Sheffield, S 3 7HF, United Kingdom.

[1] (a) Verhoeven, J. W.; Verhoeven-Schoff, A. A.; Masson, A.; Schwyzer, R. *Helv. Chim. Acta* **1974**, *57*, 2503. (b) Deranleau, D. A.; Hinman, L. M.; Coan, C. R. *J. Mol. Biol.* **1975**, *94*, 567. (c) Boranzan, H. N.; Yousif, H. A. *J. Pharm. Sci.* **1980**, *69*, 990. (d) Deranleau, D. A.; Schwyzer, R. *Biochemistry* **1970**, *9*, 126. (e) Nakano, Y.; Komiyama, J.; Iijima, T. *Colloid Polymn. Sci.* **1987**, *265*, 139.

[2] (a) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547. (b) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1550. (c) Reddington, M. V.; Spencer, N.; Stoddart, J. F. In *Inclusion Phenomena and Molecular Recognition*; Atwood, J., Ed.; Plenum Press: New York, 1990; p 41.

[3] Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396.