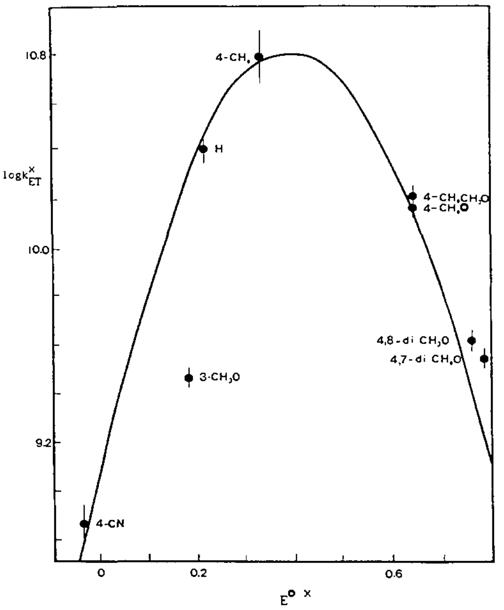

Figure 1. Plot of log $k_{ET}{}^{X}$ versus $E°{}^{X}$ of electron transfer for the conversion of the radical pair to the ion pair. The curve is a fit to eq 3 assuming log $A = 10.8$ and $\lambda = 0.39$ eV. The error bars assume a ±2% error in determination of product yields.

Using this value, the $k_{ET}{}^{X}$ values for the substrates **1a–1h** can be estimated (Table I).[17]

There has been considerable recent interest in electron transfer and, in particular, the relationship between the rate ($k_{ET}{}^{X}$) and the free energy change ($\Delta G°_{ET}{}^{X}$) for the process. Marcus theory, shown in a simple form[18] in eq 3 where λ is the reorganization

$$k_{ET}{}^{X} = A \exp\{-[\lambda(1 + \Delta G°_{ET}{}^{X}/\lambda)^2/4]/RT\} \qquad (3)$$

energy, has been particularly successful in correlations of this data. To apply eq 3 to the rates of electron transfer determined here, values of $\Delta G°_{ET}{}^{X}$ as a function of X are necessary. These can be evaluated from oxidation potential measurements according to eq 4 where the last term is the electrostatic free energy. The

$$\Delta G°_{ET}{}^{X} = E°{}^{X}(\mathrm{ACH_2^\bullet,CH_3OH}) - E°(\mathrm{PhCH_2CO_2^-,CH_3OH}) - e^2/Dr_{12} \qquad (4)$$

$$\Delta G°_{ET}{}^{X} = E°{}^{X}(\mathrm{ACH_2^\bullet,CH_3CN}) + A^{X} - E°(\mathrm{PhCH_2CO_2^-,CH_3OH}) - e^2/Dr_{12} \qquad (5)$$

$$\Delta G°_{ET}{}^{X} = E°{}^{X}(\mathrm{ACH_2^\bullet,CH_3CN}) + B \qquad (6)$$

known[9a] values for the oxidation potentials of the naphthylmethyl radicals in acetonitrile can be used, eq 5, where A^{X} is an unknown solvent correction factor. Making the reasonable assumption that A^{X} is independent of the substituent X, eq 5 simplifies to eq 6 since the last three terms are all constants. A plot[19] of log $k_{ET}{}^{X}$ versus $E°{}^{X}$ (Figure 1) shows the shape for Marcus type electron-transfer rates, including the inverted region as the process becomes prohibitively exothermic for the more easily oxidized radicals. The data apparently provide another example of this seldom, and only recently, observed phenomenon.[20,21] A value of $\lambda = 0.39$ eV gives a good fit ($s = 0.15$) to eq 3 for all the data but a much better fit ($s = 0.09$) if the point for 3-OCH$_3$ is not included.[22] Although it is possible that the 3-methoxy compound is behaving anomalously, we have no good reason for omitting it. This value of λ is small, but there is precedent for low values for electron transfer at short distances. A value of 0.48 eV has been reported for intramolecular electron transfer over 5 Å in a radical ion.[21]

Acknowledgment. We thank the NSERC of Canada for financial support, A. L. Pincock for some preliminary experiments, and D. D. M. Wayner for measuring the oxidation potentials for the naphthylmethyl radicals and for helpful discussions.

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[17] (a) Note that when $k_{ET}{}^{X}$ exceeds 10^{10} s^{-1}, cage-escape products are not observed. The diffusional escape rate in methanol is estimated at 3.5×10^9 s^{-1} assuming two spherical fragments of radius 7 Å.[17b] (b) Gardiner, W. C. *Rates and Mechanisms of Chemical Reactions*; Benjamin: New York, 1969; p 168.

[18] Reference 10, p 32.

[19] The preexponential A value, eq 3, has been set at 6×10^{10} s^{-1}.

[20] (a) Gould, I. R.; Ege, D.; Nattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794 and references therein. (b) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.

[21] Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

[22] The value of λ determines the width of the parabola, which is controlled by the magnitude of the change in $k_{ET}{}^{X}$ as a function of the change in $\Delta G°_{ET}{}^{X}$. For these substrates, k_{ET} changes by two powers of 10 as $E°$ changes from 0.72 V (X = 4-CN) to 0.35 V (X = 4-CH$_3$). The value of λ also determines, by definition, $-\Delta G°_{ET}$ at the maximum in Figure 1 and hence the constant B, eq 6, since $\lambda = E°_{max} + B$. We do not feel confident about reliably evaluating any of the three unknowns that make up B, eq 5.

Corner Flapping: A Simple and Fast Algorithm for Exhaustive Generation of Ring Conformations

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The problem of finding significantly populating conformers has been one of the major obstacles in studying conformationally flexible molecules. A number of algorithms for locating energy minima on a high-dimensional energy hypersurface have been proposed. They can be classified into two categories, random[1] and systematic.[2]

While random generation is the method of choice for macromolecules, the application of a systematic method to a chain molecule (n rotatable bonds) is severely limited due to the fact that the number of trial conformations increases at the rate of 3^n.[2a,b] However, conformational freedom is greatly reduced in *cyclic structures*, and this is where the possibility exists for developing fast methods of exhaustive conformer generation. Our new algorithm starts from any one of the known conformers and thus avoids the inherent drawback of the conventional ring-closure methods[2c,d] where the nonclosing paths must be covered at least to some depth.

The conformation of a cyclic molecule can be viewed as the up-and-down pattern of ring atoms relative to the average ring plane, ring atoms occupying "corners" of the bonds.[3] Suppose one of the ring atoms is located above the average plane. Simply

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[1] (a) Distance geometry: Crippen, G. M.; Havel, T. H. *Distance Geometry and Molecular Conformation*; John Wiley & Sons, Inc.: New York, 1988. (b) Simulated annealing: Wilson, S. R.; Cui, W.; Moskowitz, J. W.; Schmidt, K. E. *Tetrahedron Lett.* **1988**, *29*, 4373. (c) Stochastic search: Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150. (d) Ellipsoid algorithm: Billeter, M.; Howard, A. E.; Kuntz, I. D.; Kollman, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 8385. (e) Monte Carlo: Li, Z.; Scheraga, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 6611. (f) Energy-surface walking: Taylor, H.; Simmons, J. *J. Phys. Chem.* **1985**, *89*, 684. (g) Random tweak: Shankin, P. S.; Yarmush, D. L.; Fine, R. M.; Wang, H.; Levinthal, C. *Biopolymers* **1987**, *26*, 2053. (h) Random incremental pulse search: Ferguson, D. M.; Raber, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 4371. (i) Internal coordinate randomizing method: Chang, G.; Guide, W. C.; Still, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4379.

[2] (a) Tree search: Ōsawa, E.; Imai, K.; Fujiyoshi, T.; Jaime, C.; Ma, P.; Masamune, S. Submitted for publication in *J. Am. Chem. Soc.* (b) MULTIC: Lipton, M.; Still, W. C. *J. Comput. Chem.* **1988**, *9*, 343. (c) RINGMAKER: Still, W. C. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: Oxford, 1983; p 233–246. (d) Chain closure: Bruccoleri, R. E.; Karplus, M. *Macromolecules* **1985**, *18*, 2767. (e) Generic shape method: Gerber, P. R.; Gubernator, K.; Muller, K. *Helv. Chim. Acta* **1988**, *71*, 1429.

[3] This idea is independently realized and developed into a different algorithm by Gerber et al.[2e]

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J. Am. Chem. Soc. **1989**, *111*, 8951–8953

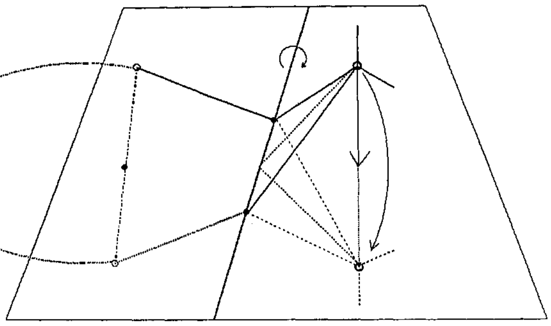

Figure 1. Illustration of corner flapping process for transforming a ring conformer. Circled atom at top right is the corner to be flapped. Two α ring atoms (solid circles) and the midpoint (solid circle) of two β ring atoms (open circles) define a plane. The corner atom is moved across the plane to the opposite side.

Table I. Performance of Corner Flapping in Generating Energy Minimum Conformations of Lower Cycloalkanes C_nH_{2n} (n = 6–14)

n	time,[a] h	N[b]
6	0.13	2 (2)
7	0.17	2 (2)
8	0.44	4 (4)
9	0.86	5 (5)
10	3.80	14 (15)
11	12.47	15 (27)
12	1.31[c]	18 (87)
13	2.24[c]	44 (116)
14	3.47[c]	44 (159)

[a] Unless otherwise noted, time is measured on a VAX Station 2000 under the single-task mode. [b] Number of conformers having Boltzmann distributions larger than 0.01%. Parenthesized is the total number of conformers generated by the corner flapping calculation. [c] Time measured on a mainframe computer (HITAC M-682).

flapping the corner atom to below the plane produces a different conformer, as we often practice with the framework molecular model. In order to program the flapping process, it is convenient to define a local plane based on several ring atoms near the corner and displace the corner atom vertically to the mirrored position on the other side of plane (Figure 1).

The flapping process is equivalent to simultaneously rotating, in disrotatory fashion, two endocyclic bonds extending from the corner atom. The new conformation thus obtained is optimized with any computational method like MM2[4] and compared with the saved conformers by conventional criteria including steric energy, dihedral angle pattern, and symmetry considerations. A structure is saved only when a new conformer is obtained, but otherwise discarded. When all the corners have been flapped, this structure is marked as *finished*. Thereupon, the most stable of the *unfinished*, saved conformers is subjected to the next flapping/minimization process. It should be noted that this algorithm does not produce a tree structure as in the other systematic algorithms, since every branch is immediately pruned to retain only the new conformer. The search terminates when all the saved conformers have been flagged as *finished*.[5]

Cycloalkanes up to a 14-membered ring were first tested (Table I). The total number of conformers and the structural details of the conformers found agree with those described by the stochastic search method.[1c] For cyclic molecules having rotatable side chains, one might assume that the attachment of side chains in all possible rotationally isomeric conformations to every possible ring conformer should produce all possible structures. The assumption is, however, unsafe in view of the recently recognized conformational coupling phenomenon.[6] Our algorithm is hence combined with the exhaustive rotation of the side chain.[2a] The program has been successfully tested for several substituted cyclohexanes.[7]

Two features of the corner flapping algorithm must be responsible for its high speed as shown in Table I. First, the flapping operation never fails to cross over the barrier separating different conformers, hence the new conformation does not return to the original one during subsequent energy minimization. Secondly, the structure is perturbed by the flapping operation only in the immediate vicinity of the corner, and the new conformation that resulted can quickly adjust itself to a new energy minimum.[8]

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Supplementary Material Available: Table of MM2-optimized Cartesian coordinates (carbon atoms only) and steric energies of all conformers listed in Table I (41 pages). Ordering information is given on any current masthead page.

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(4) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC 1982.

(5) During the whole search, the process of flapping of all corners is repeated N times, where N is the total number of conformers for the ring compound in question. If the average time of each geometry optimization is t seconds, and the number of corners in the molecule n, the computer time necessary to terminate the search is approximately equal to nNt seconds. When MM2 is used, t is 90 s for cyclodecane on VAX Station 2000. N is generally unknown, but the parenthesized N in Table I should provide some measure.

(6) Iratcabal, P.: Liotard, D. *J. Am. Chem. Soc.* **1988**, *110*, 4919.

(7) Program CONFLEX2 has been submitted to QCPE.

(8) A referee questioned the validity of our fundamental assumption that there will not be any other networks of conformers that are not connected to the one found through single flaps. We have at the moment no proof for this assumption, but our test calculations have so far reproduced all those found by random methods. As a further check, we began testing *double flaps*, wherein all pair-wise combinations of corners are flapped, and still have not found any new conformers other than those found by single flaps.

A High-Intensity Molecular Beam of Vinyl and Ethynyl Radicals

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We report a clean, high-yield, high-number-density ($>10^{14}$ cm^{-1} at the nozzle) source of vinyl (**1**) and ethynyl (**2**) radicals for gas-phase spectroscopic investigations. Supersonic jet flash pyrolysis[1] of *tert*-butyl peracrylate (**3**) and *tert*-butyl perpropriolate (**4**), seeded in a continuous helium expansion, gives near-quantitative conversion to radical products. Products and yields were probed by 10.49-eV vacuum UV laser photoionization mass spectroscopy.[2] Loss of radicals by bimolecular reactions amounted to no more than ≈20% of the nascent species. We hope to exploit the unique features of supersonic pyrolysis jets as a gas-phase analogue to cryogenic matrix isolation for the spectroscopy and energetics of organic reactive intermediates.

tert-Butyl peresters were prepared in ≈40% (for **3**) and 80% (for **4**) yield via the acid chlorides by a low-temperature Schotten–Baumen procedure.[3] Attempted carbonyldiimidazole and ethyl[3-(dimethylamino)propyl]carbodiimide (EDC) mediated couplings[3] of acrylic or propriolic acid with *t*-BuOOH were unsuccessful. Propriolyl chloride[4] was prepared by slow addition

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[†] NSF Presidential Young Investigator, David and Lucile Packard Fellow, Shell Faculty Fellow, Camille and Henry Dreyfus Distinguished New Faculty Fellow.

(1) Chen, P.; Colson, S. D.; Chupka, W. A.; Berson, J. A. *J. Phys. Chem.* **1986**, *90*, 2319.

(2) Chen, P.; Colson, S. D.; Chupka, W. A. *Chem. Phys. Lett.* **1988**, *147*, 466.

(3) For a review of perester syntheses and reactions, see: Singer, L. A. In *Organic Peroxides*; Swern, D., Ed.; John Wiley: New York, 1970; Vol. 1.

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