7-Methyl-7*H*-benzo[*c*]carbazole (7-MBC). 2-MAN (0.233 g, 0.001 mol) was dissolved in 1 L of UV-grade cyclohexane. The solution was illuminated in a Rayonet RPR-100 reactor for 15 h with "350-nm" lamps. Thirty minutes before and during illumination purified N_2 was bubbled through the solution. After evaporation of the solvent the residue was chromatographed on a SiO_2 column with cyclohexane–toluene 1:1. Two fractions (starting material and photoproduct) were collected. The photoproduct (7-MBC) was recrystallized twice from methanol and afforded 17 mg (7.4×10^{-5} mol) pale yellow crystals: mp 118 °C (lit.[17] 118–119 °C); UV_{max} (log ϵ) in MCH 369 (3.90), 362 (3.58), 350 (3.77), 327 (4.21), 315 (4.06), 288 (4.09), 267 (4.77) nm; NMR (Me_2SO-d_6) δ 8.80 (d), 8.62 (d), 8.09 (d), 8.01 (d), 7.93 (d), 7.77 (d), 7.72 (t), 7.52 (t), 7.48 (t), 7.36 (t), 4.02 (s, 3 H).

Irradiation. Spectroscopic irradiations were performed with about 5×10^{-5} M solutions in 1×1 cm^2 quartz cells. The solutions were degassed on a high-vacuum line, using the freeze–pump–thaw technique, and sealed off.

Solvents. Methylcyclohexane and isopentane (Fluka purum) were chromatographed.[16] Acetonitrile and ethanol (Uvasol Merck) were used without further purification.

Spectra. UV spectra were recorded on a Perkin-Elmer Model 320 recording spectrophotometer. Mass spectra were measured on a Varian MAT Model CH 7 instrument at 70 eV and NMR spectra on a Bruker WH 270 pulse Fourier transform (270 MHz) instrument.

Flash Photolysis. The flash apparatus has been described elsewhere.[4c] The cooling technique of Fischer[18] was applied for experiments at low temperatures. The optical path length of the flash cells was 100 mm.

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Registry No. 1-MAN, 34160-17-3; **2**-EAND, 83160-30-9; **2**-AN, 135-88-6; **2**-MAN, 6364-05-2; **2**-MANS, 64032-78-6; **7**-EBCD, 83160-31-0; **7**-BC, 205-25-4; **7**-MBC, 29103-83-1; **7**-MBCS, 83160-32-1; **9**, 54903-06-9; **10**, 83160-33-2; **11**, 83160-34-3; **15**, 83160-35-4; **16**, 5425-53-6; *N*-acetyl-2-naphthylamine, 581-97-5; bromobenzene-d_5, 4165-57-5.

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Torsional Potential Function of *n*-Butane. Correlation Effects in the Quantum-Mechanical Prediction of the Syn–Anti Energy Difference

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Abstract: Hartree–Fock–Roothaan (HFR) calculations have been carried out by using a split-valence (6-31G) basis set for the title conformations of *n*-butane. The calculated energy difference was 6.36 kcal/mol, compared to 5.99 kcal/mol reported earlier for an STO-3G basis set. (Both calculations used molecular mechanics (MM2) optimized geometries for which the energy difference is 4.73 kcal/mol.) Inclusion of polarization functions at the HFR level leaves the energy difference virtually unchanged, 6.48 kcal/mol. Configuration interaction calculations over 11 665 of 33 234 possible singly and doubly excited valence configurations reduce the energy difference to 4.58 kcal/mol.

The *n*-butane molecule is a fundamental unit, an understanding of which is required for conformational analysis of hydrocarbons. There are four important torsional extrema: 0° (syn or cis), ~60° (gauche), ~120° (eclipsed), and 180° (anti or trans). While the latter three conformations are reasonably well understood, the syn form has presented some difficulties.[2] Theoretical estimates of the syn–anti energy difference have been derived on several occasions from Hartree–Fock–Roothaan (HFR) calculations,[3] but no *direct* experimental values are available (vide infra). The most reliable (in our judgement) HFR value for this difference is 5.99 kcal/mol (STO-3G),[2] but this is significantly higher than the molecular mechanics value of 4.73 kcal/mol (MM2).[4] We do not see how the HFR value could be utilized in molecular mechanics to give reasonable results. We, therefore, concluded earlier[2] that the HFR value must be in error by ~1 kcal/mol. Such an error might be ascribed to basis set limitations, but the STO-3G basis set has seemed to be adequate for hydrocarbons in the past.[2]

Inclusion of electron correlation effects will give a lower calculated energy than the HFR formalism for a given molecule and choice of basis set. It is expected,[5] and generally found, that the energy lowering is similar for different conformations of the same molecule. It has been suggested, however, that this discrepancy between the MM2 and HFR values is due to correlation effects.[2] The near-constancy of correlation effects is a necessary condition for the validity of HFR conformational studies. This is usually assumed to hold for "simple" alkanes. Even so, recent studies of 1,2-difluoroethene have demonstrated the importance of correlation effects in accounting for the cis–trans energy difference.[6] There is reason to believe that a similar effect is operative for the syn and anti forms of *n*-butane. In the former conformation the methyl groups approach each other quite closely, well within their van der Waals radii. Their is substantial van der Waals repulsion, but masked by this is a van der Waals attraction previously estimated to be about 1 kcal/mol.[2] This dispersion energy is essentially a correlation effect, accommodated within the molecular

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Table I. Ab Initio Results for *syn*- and *anti*-Butane

calculation	basis set	E(syn), au	E(anti), au	ΔE, kcal/mol
SCF	6-31G	−157.218 797	−157.228 929	6.36
SCF	6-31G+P[a]	−157.298 189	−157.308 520	6.48
CISD[b,c]	6-31G	−157.312 984	−157.320 828	4.92
CISD[b,d]	6-31G	−157.428 038	−157.435 338	4.58

[a] Polarization functions have been added to each atom as follows: C, an sd set (0.75); H, a p set (1.00). [b] Configuration interaction over selected singly and doubly excited configurations (33 234 possible, see text). [c] 3782 configurations: the active space is MO's 5–30. [d] 11 665 configurations: the active space is MO's 5–40.

mechanics method but missing from the HFR calculations.

We report herein results of a molecular orbital (MO) study of the syn and anti conformations of *n*-butane using the split-valence 6-31G basis set.[7] The geometries used are taken from the molecular mechanics optimizations.[4] Possible basis set limitations have been further explored by carrying out HFR calculationx in which polarization functions[8] have been added to all atoms (6-31G+P). Correlations effects have been studied by the method of configuration interaction (CI). In the CI calculations (6-31G) selected singly and doubly excited configurations were included (CISD) at two different levels. In both cases all occupied valence MO's (5–17) were included. Configurations were selected by the graphical unitary group approach, the size of the calculation being controlled by truncation of the virtual space (see Table I for the virtual space truncations).[9] These results are summarized in Table I. The calculated energy difference at the HFR level is 6.36 kcal/mol for the 6-31G basis set. Addition of polarization functions induces little change in this quantity, +0.12 kcal/mol. The CISD calculations, conversely, produce a diminution of the energy difference to 4.92 kcal/mol for 3782 configurations, and 4.58 kcal/mol for 11 665 configurations. From these values we have extrapolated that the energy difference will be 4.54 kcal/mol at the CISD limit for the 6-31G basis set. We have compared these results to those obtained for ethane at the 6-31G level. The rotational barriers found for MM1[10] geometries are 2.83 kcal/mol at the HFR level and 3.03 kcal/mol for the full CISD calculation. Thus, the correlation effects that we find reflect the unique features of *syn-n*-butane. We were unable, unfortunately, to carry out CISD calculations for the butane conformations with the 6-31G+P basis set due to disk storage limitations.

It is clear that, when correlation effects are taken into account, the energy difference is predicted to match closely that obtained from the molecular mechanics studies. This is reassuring, as the large thermodynamic data base used to parameterize the molecular mechanics method made it seem unlikely that the error was in the MM2 value. Most previous estimates of this energy difference have not been helpful. Ito suggested a value of 6.1 kcal/mol,[11] but this was derived from a thermodynamic analysis assuming a planar cyclopentane. Ultrasonic relaxation studies[12] have led to a proposed value of 6.7 kcal/mol, but this value draws upon questionable data for 2-methylbutane. Durig[13] has analyzed the far-infrared spectrum of *n*-butane and derived a value of 3.02 kcal/mol for this energy difference. (This value is suspiciously low and probably reflects the limited torsional data available for the analysis.) Recent Raman studies of the relevant spectral lines at higher resolution have led to a more reasonable value, 4.52 kcal/mol.[14] This last value implies that the MM2 and CISD values probably provide the most accurate theoretical assessments of this energy difference thus far.

The significance of these results extends far beyond the case of *n*-butane itself. When molecular mechanics calculations indicate large dispersion interaction energy differences, it is quite likely that calculations at the HFR level will be in error, as for butane. This will generally be true for congested molecules. At the practical level, a simple dispersion energy calculation may suffice to overcome this difficulty. It follows that care must be exercised in the use of HFR calculations for generation of data required in the development of molecular mechanics force fields.

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Registry No. Butane, 106-97-8.

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Oxidation of Ascorbic Acid and Dehydroascorbic Acid by Superoxide Ion in Aprotic Media

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Abstract: In dimethylformamide, superoxide ion (O_2^-) oxidizes ascorbic acid (H_2A) to dehydroascorbic acid (A). The rate-limiting step is first order for each reactant and has a second-order rate constant (k) of $2.8 \times 10^4\ M^{-1}\ s^{-1}$; the overall stoichiometry is $3H_2A$ molecules per $2O_2^-$ ions. Addition of O_2^- to dehydroascorbic acid (A) results in its rapid oxidation ($k = 3.3 \times 10^4\ M^{-1}\ s^{-1}$), with an overall stoichiometry of $2O_2^-$ per A. The major products of the process are oxalate ion and the anion of threonic acid. On the basis of the reaction stoichiometries, kinetics, and products, self-consistent mechanisms are proposed for the oxidation of ascorbic acid and dehydroascorbic acid.

The oxidation of ascorbic acid (H_2A) and its anion (HA^-) by perhydroxyl radical ($HO_2\cdot$) and by superoxide ion (O_2^-) in aqueous solutions has been demonstrated to be a direct one-electron transfer process ($k_1 \sim 10^5\ M^{-1}\ s^{-1}$),[1,2]

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