rearrangement, $\Delta H_r(25\ °C) = -9.6 \pm 1$ kcal/mol, was determined calorimetrically.[16] The data reveal a large difference in $\Delta H_f°$, favoring **4b**. The underlying effects are addressed in an accompanying paper.[18]

Even in aqueous dioxane and in formic acid, **3b** reacted to give ≥95% of **4b** and ≤5% of solvolysis products.[19] The rearrangement of [3,3-²H]-**3b** afforded ≥95% of [5,5-²H₂]-**4b**, i.e., the triflate counterion returns to the same side of the molecular plane from which it departed. At elevated temperatures, **4b** solvolyzed with complete (±5%) inversion, giving rise to [6,6-²H₂]-**7**. Nucleophilic attack at the covalent substrate is most likely since no redistribution of alkoxy-¹⁸O was detected in the triflate **4b** that was recovered after 50–75% conversion. The **3b:4b** rate ratio (Table I) and the derived ratio $k_H/k_{\beta\text{-CN}} = 4 \times 10^5$ conform with previous work,[3–5] although the ionization of **3b** proceeds only to tight ion pairs, and **4b** does not ionize at all.

In order to generate the cations **1** and **2**, we resorted to dediazoniation. A modified Strecker synthesis (KCN/NH₄Cl/H₂O/MeOH, 80 °C, 16 h, 41%) converted bicyclo[2.1.1]hexan-2-one to the amino nitrile **8**, which was partially resolved (20% ee) by HPLC of the (S)-2-acetoxypropionamide.[20] Diazotization of optically active **8** (NaNO₂, dilute HClO₄, pH 3.5) produced the alcohols **7** and **5** (81:19) as racemates (0 ± 2% ee). Moreover, [3,3-²H]-**8** gave **7** with random distribution of the deuterium between positions 5 and 6 (7:7' = 1.00 ± 0.05). The amino nitrile [6,6-²H₂]-**6** was prepared from [5,5-²H₂]-**4** by displacement with lithium azide (tetraglyme, 60 °C, 20 h, 61%), followed by catalytic hydrogenation (Pd–C, ether, 92%). Diazotization of [6,6-²H₂]-**6** afforded **7** with a 3:1 distribution of the deuterium between positions 5 and 6; the product ratio **7:5** was 98.5:1.5.

The stereorandom reactions of **8** point to the achiral carbocations **1** and **2** as intermediates. Only 50% of the diazonium ions derived from **6** follow a stereorandom path (k_c), yielding **7** + **7'** and **5** in a 97:3 ratio; the remaining 50% undergo inverting displacement (k_s), leading to **7'**. With the resonable assumption that capture of the intervening carbocations is diffusion-controlled, the rearrangement **1** → **2** is found to be exothermic by 2–3 kcal/mol.

Two major conclusions may be drawn from our results: (i) The stereoselectivity of the parent 2-bicyclo[2.1.1]hexyl cation, attributed to bridging (σ delocalization),[11] is completely lost on cyano substitution. In spite of enhanced electron demand, the intermediates **1** and **2** behave as classical ions whose interconversion competes with solvent capture. (ii) In contrast to current views, the β-cyano cation **2** is more stable than the α-cyano cation **1** by 2–3 kcal/mol. The order of stabilities suggests that charge delocalization (eq 1) may not be as important as previously thought. The energy difference of the triflate precursors (9–10 kcal/mol) exceeds that of the cations. This explains why the less stable ion **1** is formed more readily, in violation of well-established rules for hydrocarbon ions.[21]

Acknowledgment. We are indebted to Professor W. R. Roth and Dr. H. W. Lennartz for the calorimetric measurements and to Professor H. Günther for some of the ²H NMR spectra. Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

(15) The rearrangement **3b** → **4b** was associated with partial scrambling of alkoxy-¹⁸O (45% in **3b** → 34% in **4b**), in close agreement with the behavior of **3a**.

(16) Solutions of **3b** in diisopropyl ether were added to nitromethane. The heat evolved was measured in a microcalorimeter[17] and corrected for the heat of mixing and the heat of solution of **4b**, determined in separate experiments.

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(19) Similar behavior has been reported for 2-(methoxycarbonyl)-2-bicyclo[2.1.1]hexyl mesylate: Della, E. W.; Elsey, G. M.; Skouroumounis, G. *Tetrahedron Lett.* **1986**, *27*, 5993.

(20) The diastereomeric (S)-2-acetoxypropionyl derivatives of **5**, **7**, and **8** were cleanly separated by GC on capillary columns (providing estimates of the ee) whereas the diastereomeric amides overlapped on HPLC (silica gel, ether–hexane, 7:3). Hydrolysis (2 N HCl, 60 °C, 3 h) of enriched amide fractions provided optically active **8** of unknown configuration.

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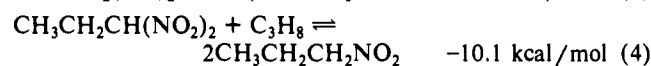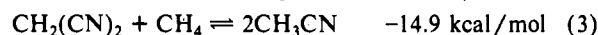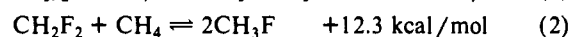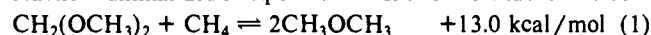
Geminal Group Interactions

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When two functional groups are attached to the same atom, they can interact with each other to cause either stabilization or destablization. This is the geminal effect.[1–4] If two substituents are both strong σ-acceptors and strong π-donors, there is a strongly stabilizing interaction, as indicated by the experimental heats of reaction summarized in eq 1 and 2.[5] If two substituents are both

$$CH_2(OCH_3)_2 + CH_4 \rightleftharpoons 2CH_3OCH_3 \qquad +13.0\ \text{kcal/mol} \qquad (1)$$

$$CH_2F_2 + CH_4 \rightleftharpoons 2CH_3F \qquad +12.3\ \text{kcal/mol} \qquad (2)$$

$$CH_2(CN)_2 + CH_4 \rightleftharpoons 2CH_3CN \qquad -14.9\ \text{kcal/mol} \qquad (3)$$

$$CH_3CH_2CH(NO_2)_2 + C_3H_8 \rightleftharpoons$$
$$2CH_3CH_2CH_2NO_2 \qquad -10.1\ \text{kcal/mol} \qquad (4)$$

σ- and π-acceptors, there is strong destabilization, as shown by eqs 3 and 4.[6] If one of the substituents is a strong acceptor and the other is a σ-acceptor but π-donor (OR, F, etc.), the two effects may compete.

In an investigation of the influence of cyano groups on cation stabilities, Kirmse and Goer determined that compound **1**, which has 1,2-disubstitution, is about 10 kcal/mol more stable than its isomer **2**, which has CN and OSO₂CF₃ (OTf) groups attached to the same carbon.[7] There could be two possible reasons for the relative stability of **1**. One is that the CN group is attached to a tertiary carbon in **1**, and this may have some special stabilizing effect; the other is that CN and OTf are both electron-withdrawing, and 1,1-disubstitution in **2** might be particularly destablizing.

1   **2**
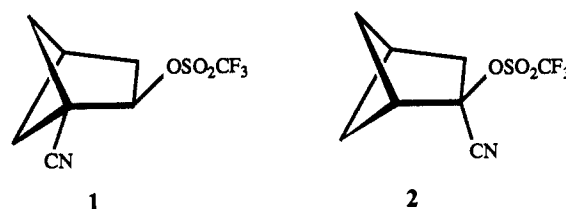
The observation is of more general significance, since the relative stabilities may influence the interpretation of substituent effects upon stabilities of reactive intermediates. In the current case, the solvolyses of **1** and **2** lead to cations substituted by cyano groups.

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Table I. Geminal Interaction Energies[a]

	3-21G	6-31G*	MP/6-31G*	exptl
CH₃CH₂CN + CH₄ ⇌ CH₃CH₃ + CH₃CN	1.5	1.0	1.9	0.8
(CH₃)₂CHCN + CH₄ ⇌ CH₃CH₂CH₃ + CH₃CN	2.8	1.3	3.5	2.5
(CH₃)₃CCN + CH₄ ⇌ (CH₃)₃CH + CH₃CN	3.7	1.3	5.0	1.8
CH₃CH₂F + CH₄ ⇌ CH₃CH₃ + CH₃F	6.3	5.7	6.7	
(CH₃)₂CHF + CH₄ ⇌ CH₃CH₂CH₃ + CH₃F	11.2	10.0	11.4	
(CH₃)₃CF + CH₄ ⇌ (CH₃)₃CH + CH₃F	14.8	13.3	16.0	

[a] In kilocalories/mole.

Table II. Geminal Interaction Energies[a]

	3-21G	6-31G*	MP2/6-31G*
CH₃CH₂OH + CH₄ ⇌ CH₃CH₃ + CH₃OH	4.9	4.1	5.4
CH₃CH₂OF + CH₄ ⇌ CH₃CH₃ + CH₃OF	5.6	4.2	5.5
CH₃CH₂OBH₂ + CH₄ ⇌ CH₃CH₃ + CH₃OBH₂	4.7	4.2	5.7
CH₂(CN)OH + CH₄ ⇌ CH₃OH + CH₃CN	-0.6	-0.9	0.0
CH₂(CN)OF + CH₄ ⇌ CH₃OF + CH₃CN	-5.7	-6.0	-4.0
CH₂(CN)OBH₂ + CH₄ ⇌ CH₃OBH₂ + CH₃CN	-3.7	-3.5	-2.9

[a] In kilocalories/mole.

An incorrect estimate of stabilities of **1** and **2** would lead to a misconception about the effect of the CN group on cation stabilities.[8,9] Similarly, the "captodative" effect, occurring when a donor and an acceptor are attached to a radical center, has been suggested to provide a special mechanism for stabilization of radicals,[10,11] but the reference system is of importance in making quantitative conclusions. To investigate such effects, we have carried out the following studies.

We explored the stabilization introduced by fluoro and cyano substitutions on propane and isobutane. We did not do calculations on OTf directly, which would be very expensive, but designed two model systems. Since Tf is both a strong σ-acceptor and a π-acceptor, we used F to model the σ-withdrawing character of Tf, and BH₂ to model the π-acceptor character of Tf.

The calculations were carried out with Pople's GAUSSIAN 86 program.[12] Geometries were fully optimized with the 3-21G and 6-31G* basis sets. Correlation energies were evaluated by second-order Moller–Plesset perturbation corrections (MP2). Calculated energies of various species are given as supplementary material. The geminal effect is calculated by isodesmic reactions as shown in Tables I and II.[13] Zero point energy corrections were not included. A positive reaction energy indicates a stabilizing geminal interaction, while a negative reaction energy indicates destabilization.

Both Me/CN and Me/F geminal interactions are stabilizing.[6] CN and F are electron-withdrawing, while Me is electron-donating. When the number of methyl substituents increases, stabilization increases in both cases. The second and the third methyl groups have slightly smaller effects than the first methyl group. The Me/CN interaction is much smaller than the Me/F interaction, consistent with the weaker inductive ability of CN com-

pared to F. The small Me/CN interaction is confirmed by experimental data, shown in Table I. The geminal interactions in propionitrile, isobutyronitrile, and pivalonitrile are 0.8, 2.5, and 1.8 kcal/mol, respectively, from experimental data,[6] whereas the best calculations indicate 1.9, 3.5, and 5.0 kcal/mol. Therefore, CN substitution at a tertiary center introduces 1–2 kcal/mol additional stabilization for compound **1** with respect to compound **2**.

The Me/OH geminal interaction is also stabilizing (Table II). When hydroxyl hydrogen is replaced by a fluorine, which increases the σ-withdrawing ability of O, there is a further increase in stabilization. The gauche conformation, **3**, is about as stable as the anti conformation, **4**. When the hydroxyl hydrogen is replaced
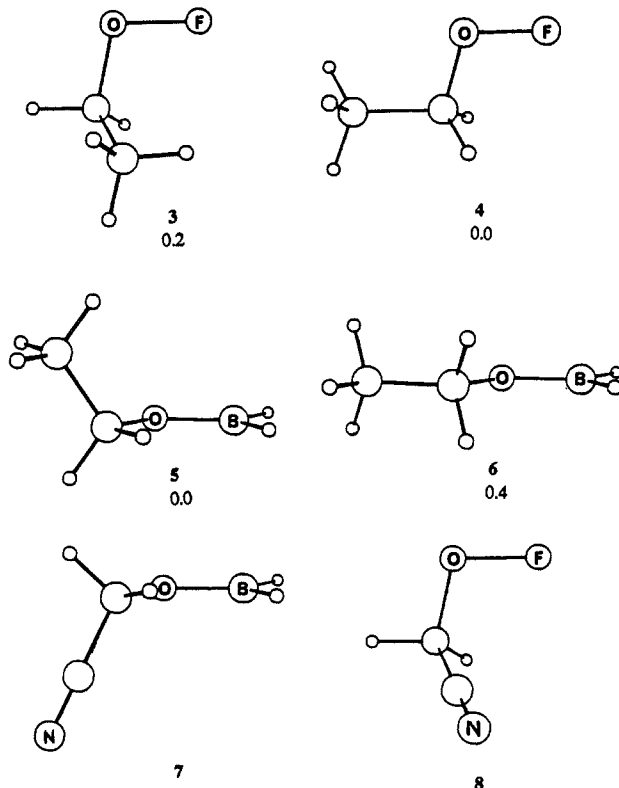
by BH₂, there is delocalization of an oxygen lone pair to a vacant p orbital on boron. The B–O bond has double-bond character, and the conformational preference about the O–C bond is similar to that of 1-butene, with a favored dihedral angle B–O–C–C of about 120°. This conformation is more stable than the anti conformation, **6**, which is the transition structure for interconversion of **5** with its enantiomer, by about 0.4 kcal/mol. Although the introduction of BH₂ reduces the π-donating ability of the

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oxygen, the geminal effect is affected very little.

When the methyl group is replaced by a CN group, there is a very small destabilizing interaction between OH and CN. Harcourt et al. estimated a 4.8 kcal/mol destabilization for the geminal interaction of CN with OH based on the equilibrium for the addition of HCN to formaldehyde,[14] whereas Beckhaus et al. found that the ΔH_f° of $(CH_3)_3CCH(OCH_3)CN$ implies no stabilizing interaction.[15] This latter result is in accord with our calculational result.

There is a significantly larger destabilizing interaction between CN and OF in 8 than between CN and OH, resulting from the increased electronegativity of OF. We also find a modest destabilizing interaction (about 3 kcal/mol) between CN and OBH_2 in 7. If we combine the effects of OF and OBH_2 to roughly model OTf, we reach the conclusion that the interaction of OTf with a strong electron-withdrawing group is significantly destablizing.[16] Returning to the relative stabilities of 1 and 2, the major factor is the geminal destabilization between CN and OTf in compound 2, which is about 7–9 kcal/mol. The remaining difference is attributed to the difference in alkyl/CN stabilization between 1 and 2, which is about 1–2 kcal/mol.

Supplementary Material Available: Table of calculated total energies of various small hydrocarbons and their F, CN, OH, OF, and OBH_2 derivatives (1 page). Ordering information is given on any current masthead page.

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(16) This model may not be adequate if the CN group is replaced by a bulky group such as CF_3, because of possible CF_3/Tf steric interactions.

Photoinduced Spin-Polarized Radical Ion Pair Formation in a Fixed-Distance Photosynthetic Model System at 5 K

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Photoinduced, multistep charge separation in bacterial reaction centers proceeds from the lowest excited singlet state of the dimeric bacteriochlorophyll electron donor in two steps, to yield a weakly interacting dimer cation–quinone anion radical pair, P^+-Q^-, separated by 28 Å.[1] The chromophores within the reaction center are positioned at precise distances and orientations to ensure that the electronic coupling between P^+ and Q^- is sufficiently weak to allow P^+-Q^- to live for about 100 ms.[2] At long distances, the electron–electron exchange interaction, J, between radicals within a charge-separated ion pair is sufficiently weak that differences in local magnetic fields surrounding each radical result in S–T₀ mixing of the radical-pair spin sublevels.[3] This mixing produces
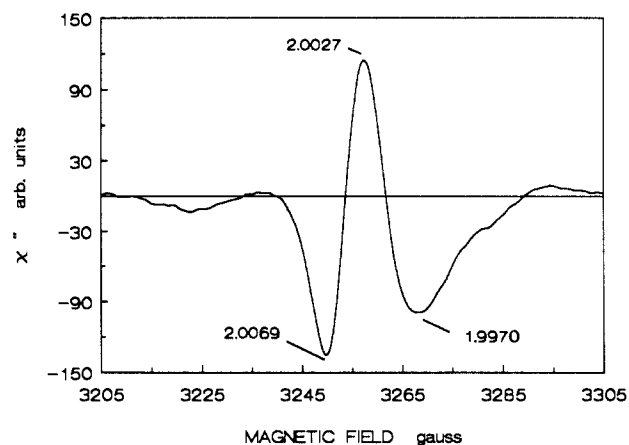
Figure 1. Integrated EPR signal of the spin-polarized radical ion pair resulting from irradiation of 5×10^{-5} M 1 in butyronitrile at 5 K using 540-nm light, modulated at 500 Hz, with lock-in detection: microwave power 5 mW, $\nu = 9.13$ GHz, Varian E-9 EPR spectrometer.

a non-Boltzmann population of the spin sublevels of the radical pair and may result in the appearance of spin-polarized EPR spectra. Such spectra have been reported extensively for both bacterial and green-plant reaction centers,[4–6] but have not been observed previously in rigid model systems. Recently, we developed criteria for achieving high quantum yield charge separation in porphyrin-based donor–acceptor systems at cryogenic temperatures.[7] Using this information as a predictive model, we synthesized compound 1, TAPD–ZP–NQ, which consists of a zinc porphyrin primary electron donor, ZP, positioned between a naphthoquinone electron acceptor, NQ, and an N,N,N,N-tetra-alkyl-p-phenylenediamine secondary electron donor, TADP. Compound 1 undergoes two-step, sequential charge separation at 5 K to yield a radical ion pair that possesses an overall 23-Å center-to-center distance,[8] *a 4-ms lifetime*, and *spin polarization* as indicated by EPR.

Compounds 1 and 2 were prepared as follows: 2-formyl-triptycenonaphthoquinone,[9] 3,3'-diethyl-4,4'-dimethyldipyrryl-methane,[10] and 5-formyl-N-(p-nitrophenyl)isoindoline[11] were condensed in CH_2Cl_2 with $BF_3 \cdot Et_2O$ catalyst[12] to yield the statistical mixture of porphyrinogens. The porphyrinogens were oxidized to porphyrins with chloranil at room temperature and separated on silica gel. The nitro group was reduced with $SnCl_2$/HCl and dimethylated with $NaBH_3CN/CH_2O$,[13] to give 2 in 15% overall yield based on the starting aldehydes (mass spectrum: FAB calcd 1047, found M + 4 1051). The porphyrin was metalated quantitatively with $ZnOAc_2$ in $CHCl_3$/MeOH to yield 1. Compound 3 was prepared in 11% overall yield by a

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