necessary to describe the electronic structure of our molecules.

We are thus led to a new picture of 1,4-disubstituted benzenes with a π donor and a nitro group: while an interaction between both groups does exist (as proved by the non-additivity of ^{13}C shifts at ipso positions), it does not go through a charge transfer from one substituent to the other one, but rather through a charge transfer to the ring, inducing a polarization of the π system of the nitro group.

Thus, our calculations support Lipkowitz's proposal of the predominance of **6** over **7**. However, it should be emphasized that this is not contradictory with the results of FRS's experiments, whose validity is not in doubt. Rather, we interpret the calculated and experimentally observed accumulation of charge on the outer oxygens, under the influence of π-donor para substituents, in a way which departs from the traditionally accepted view, since we show that charge transfer to the ring is necessary and sufficient to account for all experimental data.

Lastly, it should be kept in mind that the discussion presented in this paper applies to molecules in the gas phase. Using a polar solvent like acetonitrile, as FRS did, should certainly increase the structural weights of **6** and **7**, and probably that of **7** more than that of **6** since in the former the negative charges are exposed to solvent effects more than in the latter. These intuitive predictions are supported by the experimental finding that the influence of solvent polarity on ^{13}C shifts is not negligible,[38] and the same should hold true for ^{15}N and ^{17}O as well. Also, in proton–donor solvents, structure **7** is favored, as shown by UV spectroscopy.[39] Thus, our conclusions invalidating the classical interpretation of the "through-resonance" effect should be tempered when polar solvents are employed.

Acknowledgment. Professor J. Jullien is gratefully acknowledged for a fruitful discussion.

Registry No. *p*-Nitroaniline, 100-01-6; *p*-nitrophenol, 100-02-7.

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(38) J. Bromilow, R. T. C. Brownlee, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 2020 (1976).

(39) M. J. Kamlet. E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

Electron-Transfer-Sensitized C–C Bond Cleavage. Facile Homolytic Fission via Geminate Back Electron Transfer in Photogenerated Ion Pairs[1]

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Abstract: Several organic substrates (donors) known to undergo oxidative C–C bond cleavage upon steady-state irradiation under electron-transfer photosensitization have been examined by 337.1 nm laser flash photolysis for photoproduction of substrate radicals/radical cations and sensitizer triplet as a result of charger-transfer interaction with 1,4-dicyanonaphthalene (DCN) singlet (acceptor). The transient-absorption phenomena and quantitative estimates of electron-transfer-mediated yields show that for substrates such as 1-(diphenylmethyl)cyclohepta-2,4,6-triene and aryl-substituted pinacols and pinacol–ethers characterized by relatively unstable, short-lived, radical cations, a substantial fraction of arylmethyl radicals are generated fast via back electron transfer in the photogenerated ion pair. In other cases, we have observed longer lived radical cations (solvated) that either undergo intramolecular electron transfer leading to C–C bond fragmentation (e.g., with 1,1,2,2-tetraphenylethane) or diffusional back donation of electron from the DCN radical anion (e.g., with *p*-methoxy- and *p*-methyl-substituted bibenzyls). Within small groups of closely related quenchers, radical and radical ion yields are found to depend systematically on the structures, chemical nature, and oxidation potentials of the substrates.

In electron transfer (ET) sensitized photoreactions involving organic substrates in a polar medium, important roles are usually played by ET-derived radical ions (solvated). While fast chemical transformations in the form of isomerization and bond cleavage can occur in short-lived primary intermediates such as exciplexes[3] and ion pairs (solvent shared),[3] the solvated radical ions usually enjoy longer lifetimes and hence are susceptible to various bimolecular reactions as well as back donation of electron at the time scale of diffusion. In many instances, intramolecular ET occurs within the radical ion leading to cleavage of a relatively weak bond and consequent formation of a radical and an ion with lifetimes and chemical affinities different from those of the parent species. Studying the kinetic and spectral behaviors of transient radicals and radical ions and modes of their generation following photoexcitation is an integral part of understanding the mechanisms of photosensitized organic reactions[4] involving charge-transfer interactions.

Oxidative C–C bond cleavage effected by ET to excited-state cyanoaromatics (acceptors) is well-recognized.[4] In a recent paper,[5] we have presented a detailed account of 1,4-dicyanonaphthalene (DCN) sensitized steady-state photolyses of several systems containing C–C bonds flanked by aryl substituents. We have shown that the yields of final photoproducts (aldehydes/ketones)

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(3) (a) Gordon, M. S., Ware, W. R., Eds. "The Exciplex"; Academic Press: New York, 1975. (b) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, pp 1–78. (c) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312–318.

(4) A cross section of references for electron transfer sensitized photoreactions is the following: (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80–86. (b) Albini, A.; Arnold, D. A. *Can. J. Chem.* **1978**, *56*, 2985–2993. (c) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663–664. (d) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931–5937. (e) Padwa, A.; Chou, C. S.; Reiker, W. F. *J. Org. Chem.* **1980**, *45*, 4555–4564. (f) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455–6456. (g) Hixson, S. S.; Boyer, J.; Gallucci, C. *J. Chem. Soc., Chem. Commun.* **1974**, 540–542. (h) Davis, H. F.; Das, P. K.; Griffin, G. W.; Timpa, J. D. *J. Org. Chem.* **1983**, *48*, 5256–5259.

(5) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Eğe, S. *Can. J. Chem.* **1984**, *62*, 424–436.

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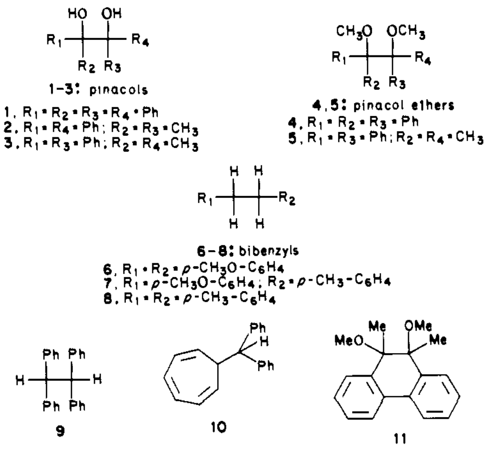
Chart I. Organic Substrates under Study (Pinacol **3** and Pinacol Ethers **5** and **11** Were Used as Racemic Mixtures)



arising from C–C bond fragmentation in the presence and, in some cases, absence of oxygen are very high. In this paper we are presenting the results of a nanosecond laser flash photolysis study of some of these systems; this has revealed a novel facet in the related ET-sensitized photoreactions, that is, fast and pronounced formation of arylalkyl radicals through homolytic cleavage of the C–C bond apparently via back donation of an electron in photogenerated ion pairs. The various relevant steps in the reaction scheme are shown below (S ≡ substrate, R· ≡ radical from C–C bond fragmentation, and R^+ ≡ corresponding carbocation)

$$ {}^1\mathrm{DCN} \rightarrow {}^1\mathrm{DCN}^* \tag{1} $$

$$ {}^1\mathrm{DCN}^* \xrightarrow{1/\tau_F} {}^1\mathrm{DCN},\ {}^3\mathrm{DCN}^*,\ h\nu_F \tag{2} $$

$$ {}^1\mathrm{DCN}^* + \mathrm{S} \xrightarrow{k_q^F} {}^1(\mathrm{DCN}^{-}\cdot \ldots \mathrm{S}^{+}\cdot) \tag{3} $$

$$ {}^1(\mathrm{DCN}^{-}\cdot \cdots \mathrm{S}^{+}\cdot) \rightarrow {}^1\mathrm{DCN} + \mathrm{S} \tag{4a} $$

$$ \rightarrow {}^3\mathrm{DCN}^* + \mathrm{S} \tag{4b} $$

$$ \rightarrow \mathrm{DCN}^{-}\cdot + \mathrm{S}^{+}\cdot \tag{4c} $$

$$ \rightarrow {}^1\mathrm{DCN} + 2\mathrm{R}\cdot \tag{4d} $$

$$ \mathrm{S}^{+}\cdot \rightarrow \mathrm{R}\cdot + \mathrm{R}^{+} \tag{5} $$

$$ \mathrm{S}^{+}\cdot + \mathrm{DCN}^{-}\cdot \rightarrow \mathrm{S} + {}^1\mathrm{DCN} \tag{6} $$

$$ \mathrm{R}^{+} + \mathrm{DCN}^{-}\cdot \rightarrow \mathrm{R}\cdot + {}^1\mathrm{DCN} \tag{7} $$

The organic substrates (ground state donors) under study are shown in Chart I.

Experimental Section

The sources and syntheses of organic substrates **1–11** (Chart I) and photosensitizer DCN are described in previous papers.[5,6] β-Carotene (Aldrich) was recrystallized thrice from 1:1 methanol:chloroform. Acetonitrile (Aldrich, gold-label) was distilled in an atmosphere of nitrogen. In all measurements, DCN concentrations were in the range 0.2–0.4 mM and the substrate concentrations were ≤30 mM. Unless the effect of oxygen was meant to be studied under air or O_2 saturation, the solutions for photolysis were deoxygenated by flushing with argon (10–20 min) presaturated with the solvent.

The steady-state emission-spectral measurements were carried out with 1 cm × 1 cm quartz cells in an SLM spectrofluorimeter. The essential features of this apparatus are given elsewhere.[7] A right-angle configuration was used for excitation and emission. All of the laser flash photolysis experiments were performed by using, for excitation, nitrogen laser pulses (337.1 nm, ~8 ns, 2–3 mJ) from a Molectron UV-400 laser system. The description of the kinetic spectrophotometer and data collection/processing system is available in previous publications[7-9] from the Radiation Laboratory. For controlling experiments and for collecting and processing data, the setup is interfaced with an LSI-11 microprocessor from which the data are transferred to a time-shared PDP 11/55 computer for storage and further analysis. For laser flash photolysis, rectangular quartz cells with 2-mm path length along and optically flat surfaces across the direction of the monitoring light were used. The exciting laser pulses intersected the monitoring light beam at ~20° (within the photolysis cell) from the side of the analyzing monochromator.

For the determination of Stern–Volmer constants ($K_{SV}{}^F$) for DCN fluorescence quenching, the intensity (I) of steady-state fluorescence at the maximum (380 nm) was measured as a function of substrate (quencher) concentration, [Q], in the range 0–15 mM; the wavelength for excitation in these experiments was 340 nm. Reasonably linear plots were obtained on the basis of the equation $I_0/I = 1 + K_{SV}{}^F[Q]$ where I_0 denotes fluorescence intensity in the absence of a quencher. The ET-derived yields of DCN radical anion (δ_{anion}), DCN triplet (δ_T), and substrate-derived radicals ($\delta_{R\cdot}$) were measured by laser flash photolysis relative to the intrinsic triplet yield ($\phi_T{}^0$) of DCN. The following equations were employed:

$$ \delta_{\mathrm{anion}} = \phi_T{}^0 \left(\frac{\Delta \mathrm{OD}_{\mathrm{anion}}}{\Delta \mathrm{OD}_T{}^0} \right) \left(\frac{\epsilon_T}{\epsilon_{\mathrm{anion}}} \right) \left(\frac{1 + K_{SF}{}^F[Q]}{K_{SV}{}^F[Q]} \right) \tag{8} $$

$$ \delta_T = \left(\frac{\phi_T{}^0}{K_{SV}{}^F[Q]} \right) \left[(1 + K_{SV}{}^F[Q]) \left(\frac{\Delta \mathrm{OD}_T}{\Delta \mathrm{OD}_T{}^0} \right) - 1 \right] \tag{9} $$

In these equations, ϵ's and ΔOD's are extinction coefficients and end-of-pulse absorbance changes, respectively, and the upper superscript zero denotes the absence of a quencher. The equation for $\delta_{R\cdot}$ is analogous to that for the anion (eq 1). The DCN triplet and radical anion (DCN^-) were monitored at their absorption maxima,[5,10] namely, 455 ($\epsilon_T = 7.0 \times 10^3$ M^{-1} cm^{-1}) and 390 nm ($\epsilon_{\mathrm{anion}} = 2.2 \times 10^4$ M^{-1} cm^{-1}), respectively. The extinction coefficients ($\epsilon_{R\cdot}$ at 325–328 nm) of diphenylalkyl radicals ($Ph_2\dot{C}R$, R = OH, OCH_3, H) derived from **1**, 4, **9**, and **10** were taken to be the same as that for $Ph_2\dot{C}OH$ ($\epsilon_{R\cdot} = 3.0 \times 10^4$ M^{-1} cm^{-1})[11] in 1:9 water:acetonitrile (v/v). For extinction coefficients ($\epsilon_{R\cdot}$ at 275–280 nm) of methylphenylalkyl radicals, namely, $Ph(CH_3)\dot{C}R$ (R = OH, OCH_3), derived from acetophenone-related pinacols (**2** and **3**) and pinacol ether (**5**), use was made of $\epsilon_{R\cdot}$ (2.9×10^4 M^{-1} cm^{-1} at 273 nm)[11b] measured for $Ph(CH_3)\dot{C}OH$ by pulse radiolysis in water. It should be noted that large uncertainties (ca. ±30%) in $\delta_{R\cdot}$ data may stem from the variation of $\epsilon_{R\cdot}$'s with respect to solvent conditions and substituents, R (H, OH, or OCH_3). For a given substrate, δ values measured at three to four different concentrations (3–15 mM) were found to agree with one another within experimental errors (±20%).

Under the condition of quenching by some of the substrates, the monitoring of the DCN triplet at 455 nm suffers from the complication of nonnegligible contribution to the transient absorbance from the radicals or radical cations derived from the substrates. This is particularly serious because the DCN triplet has a relatively small extinction coefficient (7.0×10^3 M^{-1} cm^{-1})[6,10] at its maximum in the visible (455 nm). In order to circumvent this difficulty, experiments were done in the presence of ~5×10^{-6} M β-carotene, the latter serving as a triplet counter. At a given β-carotene concentration, a constant fraction of DCN triplets produced in the presence and absence of quenchers transferred their energy to the polyene acceptor and the triplet of the latter was monitored in terms of its strong absorbance ($\Delta \mathrm{OD}_{\beta\text{-car}}{}^{\max}$) at 515 nm ($\epsilon_T = 2.4 \times 10^5$ M^{-1} cm^{-1} in hexane)[12] at the maximum of its formation–decay profile. These $\Delta \mathrm{OD}_{\beta\text{-car}}{}^{\max}$ values were then used in place of $\Delta \mathrm{OD}_T$'s in equation 9.

Results

The data concerning ET-derived yields (δ's) of photoproducts ($DCN^-\cdot$, R· and ${}^3DCN^*$, see eq 1–4) and Stern–Volmer constants

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(6) Davis, H. F.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 2798–2803.

(7) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4507–4514.

(8) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970.

(9) Das, P. K.; Bobrowski, K. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1009–1927.

(10) Das, P. K.; Muller, A. J.; Griffin, G. W. *J. Org. Chem.* **1984**, *49*, 1977–1985.

(11) (a) Baral-Tosh, S.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 1404–1408. (b) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072–2078.

(12) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

Table I. Stern–Volmer Constants for DCN Fluorescence Quenching and Yields of Electron-Transfer-Derived Products (Solvent: Acetonitrile)

sub-strate	$K_{SV}{}^{F}$,[a] M^{-1}	$\tau_{R\cdot}$,[b] μs	δ_{anion}[c]	$\delta_{R\cdot}$[c]	δ_T[d]
1	115	0.17	0.15	1.0	0.21, 0.16[e]
2	103	0.32	0.07	0.19	0.12, 0.05[e]
3	94	0.34	≤0.05	0.12	<0.05
4	118	0.43	0.31	1.7	<0.05
5	79	0.17	0.14	0.76	<0.05
6	161		0.22		0.07
7	125		0.26		0.10
8	118		0.67		0.16
9	94	0.35	0.59	0.83	0.12
10	138	0.37	0.08	0.42	<0.05[e]
11	144		0.40		0.18

[a] ±15%. [b] In air-saturated acetonitrile; monitored at 325–328 nm for $Ph_2\dot{C}H$ and $Ph_2\dot{C}OR$ and 275–280 nm for $Ph(CH_3)\dot{C}OR$; ±15%. [c] ±20%. [d] ±30%. [e] These values were obtained by assuming that the end-of-pulse absorbance at 455 nm was entirely due to the DCN triplet.

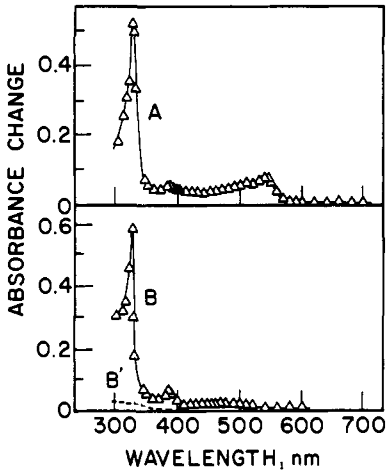

Figure 1. Transient absorption spectra observed at ~0.5 μs following 337.1-nm laser flash photolysis of DCN (0.38 mM) under quenching by (A) pinacol **1** (10.5 mM) and (B) pinacol ether **4** (15.0 mM) in deaerated acetonitrile. The broken curve B′ represents the transient spectrum at 3 μs following laser flash in air-saturated acetonitrile containing 0.35 M DCN and 10.7 mM **4**.

($K_{SV}{}^{F}$) for DCN fluorescence quenching are presented in Table I. The K_{SV} F data coupled with the DCN singlet lifetime (τ_F), 9.5 ns in acetonitrile,[10] give the bimolecular rate constants, $k_q{}^{F}$ ($=K_{SV}{}^{F}/\tau_F$), in the range 0.8–1.5 × 10^{10} M^{-1} s^{-1} (that is, in the limit of diffusion control). Irreversibility of electron transfer, implied in eq 3 and used in deducing eq 8 and 9, is justified under this condition.

The transient absorption spectra at 300–700 nm observed upon laser flash photolysis of DCN in acetonitrile under ~60% singlet quenching by benzopinacol and benzopinacol ether are shown in Figure 1, parts A and B, respectively. Both spectra are dominated by a sharp and intense peak at 325–328 nm, characteristic of diphenylmethyl-type radicals. Furthermore, in the case of the pinacol nFigure 1A), a minor band system is observed at 480–580 nm (λ_{max} = 545 nm), the maximum absorption intensity in this region being about eight times smaller than that at 328 nm. The close resemblance of the spectrum comprising the two band systems at 300–350 and 480–580 nm with that of the diphenylhydroxymethyl radical[11] suggests that the cleavage of the C–C bond in the pinacol occurs fast following photoexcitation, producing the ketyl radical. Confirmation of the assignment as the ketyl radical is obtained from the agreement of lifetime (0.17 μs) observed for the decay of transient absorption at 328 and 545 nm in air-saturated solution with that of $Ph_2\dot{C}OH$ produced from benzophenone triplet by hydrogen abstraction from *p*-methoxyphenol under identical conditions. By analogy, the transient absorption at 300–350 nm in the case of benzopinacol ether (Figure 1B) is assigned to $Ph_2\dot{C}OCH_3$, produced via fast bond cleavage (see below) in the radical cation.

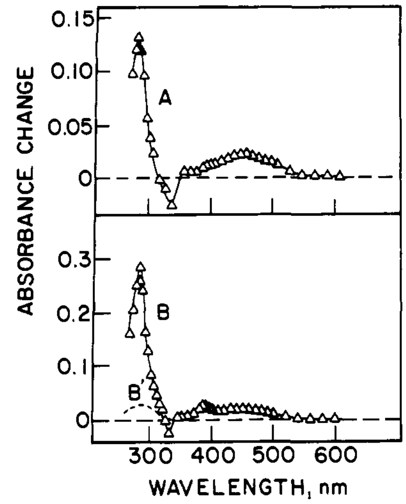

Figure 2. Transient absorption spectra observed at ~0.5 μs following laser flash photolysis of DCN (0.35 mM) in the presence of (A) pinacol **2** (9.4 mM) and (B) pinacol ether **5** (12.6 mM) in deaerated acetonitrile. The broken curve B′ is the spectrum at 3 μs following laser flash in air-saturated acetonitrile containing 0.35 mM DCN and 12.6 mM **5**.

In addition to the transient absorption associated with the radicals $Ph_2\dot{C}OR$ (R = H, CH_3), a minor peak is observed at 390 nm in both cases, see Figure 1, parts A and B. This is attributable to the DCN radical anion (DCN^{-}).[10] When one considers the fact that the extinction coefficient of $Ph_2\dot{C}OH$ (3.0 × 10^4 M^{-1} cm^{-1})[11] at 328 nm is only ~40% larger than that of $DCN^{-\cdot}$ (2.2 × 10^4 M^{-1} cm^{-1}) at 390 nm, it becomes clear that the yield of ketyl radical in the case of benzopinacol is about seven times greater than that of DCN^{-}. A similar ratio (~6) is also obtained for benzopinacol ether if one assumes that the extinction coefficient of $Ph_2\dot{C}OCH_3$ at 328 nm is the same as that of $Ph_2\dot{C}OR$. In spite of uncertainties in ε values, the results show that the radicals are formed in much larger yields than expected from the dissociation of the radical cation ($S^{+\cdot}$) formed in an amount equivalent to that of DCN^{-} (eq 4c and 5). Thus, we are led to believe that the radicals are produced via back-electron transfer within the photogenerated ion pair (eq 4d). It is highly unlikely that the carbocations $Ph_2C^{+}OR$ have very intense absorption spectra matching those of $Ph_2\dot{C}OR$ and thus explain the discrepancy regarding the lack of equivalence between the observed absorptions of DCN^{-} and $Ph_2\dot{C}OR$. Oxygen is not expected to affect the decay of the cationic species, $Ph_2C^{+}OCH_3$ and $Ph_2C^{+}OH$, the latter being the protonated form of benzophenone. The transient spectra following the decay of the radicals in air-saturated solutions show a weak, slowly decaying, residual absorption at 300–350 nm (see Figure 1B′); this is possibly due to the carbocation formed in an amount equimolar to that of DCN^{-}. The fact that no relatively slow growth component is observed at 325–328 nm in deoxygenated solutions at the time scale of decay of solvated DCN^{-} suggests that back-electron donation from DCN^{-} to carbocations to give radicals (eq 7) does not occur (unless R^{+} and $R^{\cdot}$ have equal extinction coefficients). Furthermore, the dissociation of the radical cations ($S^{+\cdot}$) of benzopinacol and benzopinacol ether into radicals and cations (eq 5) occurs within nanoseconds following their escape from the cage.

The observations with pinacols (**2** and **3**) and pinacol ether (**5**) derived from acetophenone are similar to those with benzopinacol and benzopinacol ether. These are illustrated in Figure 2. The radicals $Ph(CH_3)\dot{C}OR$ (R = CH_3, H) exhibit their sharp maxima at 275–280 nm; since the DCN triplet also has a sharp maximum[10] at 275 nm, thrice as intense as that at 455 nm, the absorbance at 275–280 nm was corrected for the contribution from the DCN triplet by extrapolation from the absorbance at 455 nm (where $Ph(CH_3)\dot{C}OH$ and, by analogy, $Ph(CH_3)\dot{C}OCH_3$ have no significant absorption).[11b] The apparent discrepancy in $\delta_{R\cdot}$ and δ_{anion}

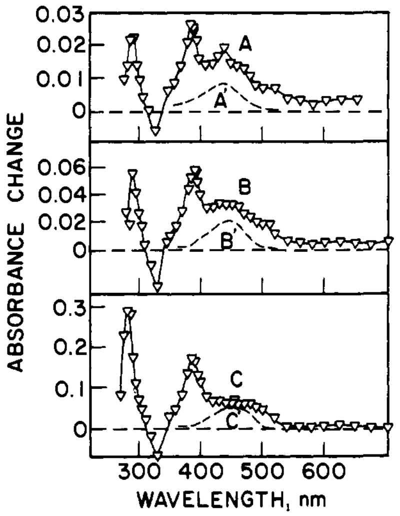

Figure 3. Transient absorption spectra observed at 0.5 μs following laser flash photolysis of DCN (0.25 mM) in the presence of (A) 12.4 mM **6**, (B) 15.9 mM **7**, and (C) 30 mM **8** in deaerated acetonitrile. The broken curves A'–C' represent spectra at 2.5 μs after laser flash in air-saturated solutions, other conditions being the same as in deaerated acetonitrile.

is less spectacular for the pinacols **2** and **3** than for **1**, **4**, and **5**. The oxygen-insensitive carbocations $Ph(CH_3)C^+OR$ (R = H, CH_3) appear to absorb at 260–310 nm (see Figure 2B').

With methyl- and methoxy-substituted bibenzyls, **6** and **7**, C–C bond fragmentation does not seem to occur at initial stages following photoinduced ET from these substrates. The transient absorption spectrum in each case (Figure 3) is a superimposition of the spectra of DCN^{-} (λ_{max} = 390 nm) and the corresponding bibenzyl radical cation (λ_{max} = 430–440 nm). In the spectral region 400–500 nm, the overlap with the spectrum of the DCN triplet is serious, but the spectra due to the radical cations could be isolated by quenching the former with β-ionone ($k_q^T = 1.3 \times 10^9$ M^{-1} s^{-1}) or oxygen ($k_q^T = 2.1 \times 10^9$ M^{-1} s^{-1}). The radical cation spectra in air-saturated solutions (Figure 3A'–C') match well with those observed for *p*-xylene and *p*-methoxytoluene radical cations.[13] That the end-of-pulse absorbances at 410–470 nm observed upon laser flash photolysis of DCN in the presence of bibenzyls are primarily due to radical cations, rather than the DCN triplet, is corroborated by the following. The ET-mediated triplet yields (ϕ_T) determined by the β-carotene counting technique (see Experimental Section) are 2–3 times smaller than those calculated on the basis of an assumption that the absorbance at 455 nm is entirely due to the DCN triplet. It is important to note that no significant absorbance change is noted at 300–320 nm on a nanosecond or microsecond time scale that could be attributed to *p*-methyl- or *p*-methoxybenzyl radicals formed as a result of back-electron donation in the ion pair (eq 4d) or between the solvated radical ions (eq 6); the benzyl radicals are known[14] to have sharp absorption maxima at 310–320 nm ($\epsilon = 9.0 \times 10^3$ M^{-1} cm^{-1} for $PhCH_2\cdot$ at 318 nm in water).[14a]

With 1,1,2,2-tetraphenylethane (**9**) we come across an interesting situation. In this case, nearly all of the transition absorption due to $Ph_2CH\cdot$ at 325 nm is associated with a relatively slow formation process (τ = 160 ns), see the inset of Figure 4. The transient spectra (Figure 4A) show the formation of both $Ph_2CH\cdot$ and DCN^{-} in yields that are relatively high (0.6 and 0.8) as well as nearly equivalent. In contrast to the slow formation of $Ph_2CH\cdot$, that of DCN^{-} occurs within nanoseconds after the laser pulse. These observations show that intramolecular ET leading to dissociation (eq 5) occurs rather slowly in the radical cation of **9** following its escape from the solvent cage. The carbocation,

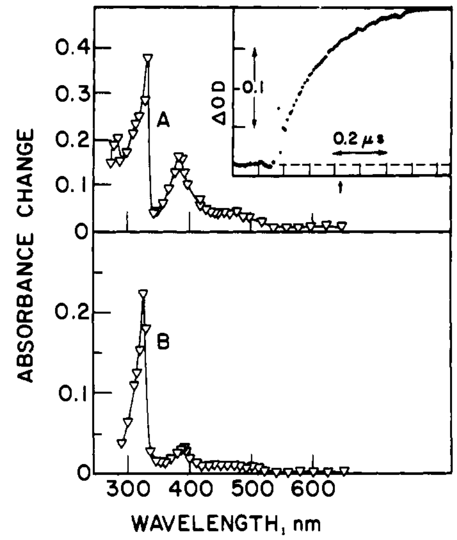

Figure 4. Transient absorption spectra observed at 1 μs following flash photolysis of 0.25 mM DCN in deaerated acetonitrile containing (A) 22.9 mM **9** and (B) 18.9 mM **10**. Inset: kinetic trace at 325 nm in deoxygenated acetonitrile solution containing 0.35 mM DCN and 9.4 mM **9**.

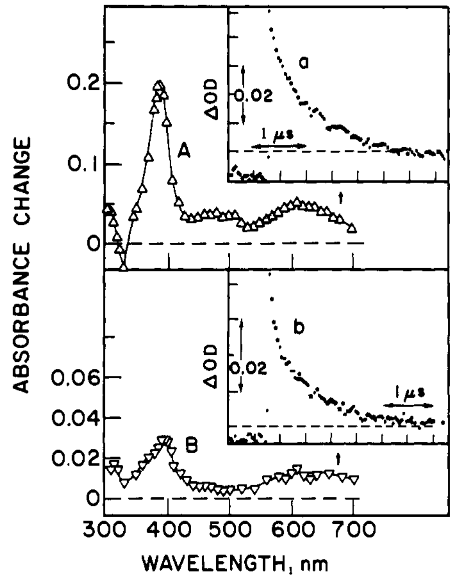

Figure 5. Transient spectra at 1 μs following laser flash photolysis of 0.38 mM DCN in the presence of 16.8 mM **11** under (A) deaerated condition and (B) air saturation. Insets: kinetic traces at 610 nm observed for 0.35 mM DCN + 11.6 mM **11** under (a) deaerated condition and (b) air saturation.

Ph_2C^+H, absorbing[15] at 400–500 nm (λ_{max} = 445 nm in 1,2-dichloroethane)[15a] and quenchable by Br^-, also shows a growth component. Unfortunately, because of strong overlap with the DCN triplet absorption, no reliable kinetic data could be obtained for Ph_2CH^+ under the conditions of our experiments.

With the cycloheptatrienyl derivative **10** as the substrate (Figure 4B), the yield of DCN^{-} is very small (0.08) although the yield of $Ph_2\dot{C}H$ (assumed to be solely responsible for the transient absorbance at 328 nm) is about five times larger. The major part (>90%) of the absorbance at 328 nm under >50% quenching of the DCN singlet is produced fast (i.e., within nanoseconds from the laser pulse), indicating rapid C–C bond fission via back ET in the ion pair (eq 4d) and to a small extent in the form of rapid dissociation of solvated radical cation (eq 5). Under conditions

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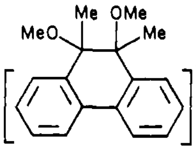
[13] Davis, H. F.; Chattopadhyay, S. K.; Das, P. K., in preparation.

[14] (a) Mittal, J. P.; Hayon, E. *Nature (London)* **1972**, *240*, 20–21. (b) Izumida, T.; Ichikawa, T; Yoshida, H. *J. Phys. Chem.* **1980**, *84*, 60–63. (c) Hiratsuka, H.; Okamura, T.; Tanaka, I.; Tanizaki, Y. *J. Phys. Chem.* **1980**, *84*, 285–289.

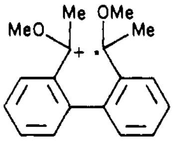
[15] (a) Dorfman, L. M.; DePalma, V. M. *Pure Appl. Chem.* **1979**, *51*, 123–129. (b) In concentrated sulfuric acid, the carbocation $Ph_2(CH_3)C^+$ exhibits a maximum at 430 nm (log ϵ_{max} = 4.5). See: Gold, V.; Tye, F. L. *J. Chem. Soc.* **1952**, 2172.

of small extent of quenching (i.e., low [Q]), a growth component (minor) is observed at 300–330 nm. However, the kinetics of this process at varying [Q] correspond to those of the decay of the DCN triplet (at 455 nm), the latter being quenched by the substrate (a cyclic triene) by energy transfer ($k_q{}^T \sim 1 \times 10^9$ M^{-1} s^{-1}). We interpret the growth component of transient absorption at 300–330 nm as the formation of $Ph_2CH\cdot$ by rapid fragmentation[16] of the triplet of **10**, the latter resulting from energy transfer sensitization by the DCN triplet.

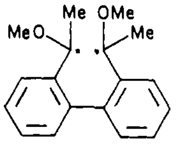
Sorting out the transient phenomena (Figure 5) observed upon laser flash photolysis of DCN under quenching by the cyclic pinacol ether (**11**) is complicated by the fact that the absorption spectrum of DCN^- at 380–400 nm overlaps strongly with a nearly identical band system of the radical cation from **11** in this region. As shown by the spectra in air-saturated solution (Figure 5B) in which DCN^- is quite short lived (τ = 54 ns),[10] there is a second absorption band system at long wavelengths (550–700 nm); when measured close to the laser pulse, the absorption intensity at the long-wavelength maximum (640 nm) is 2.6 times smaller than that at the short-wavelength one (395 nm). The contribution of the radical cation of **11** at 390 nm was corrected for in calculating δ_{anion} based end-of-pulse absorbance at this wavelength (see Experimental Section). The obvious question is whether the observed spectrum corresponds to a biphenyl-like, closed-ring species (I) or an open-ring, radical-cum-carbocation (II). It is noted that the observed spectrum resembles closely that of the biphenyl radical cation[17] (λ_{max}'s = 380 and 660 nm in water)[17a] in terms of the presence of two maxima as well as their relative intensities at the early stage after formation. This suggests that $S^{+\cdot}$ in the case of **11** is originally in the ring-closed form (I). The decay kinetics of transient absorption, shown in the insets of Figure 5, is complex in both deoxygenated and air-saturated solutions; it is comprised of an initial, fast decay (over ~5 μs in a degassed solution) followed by a slower, second-order-like decay over >100 μs. The decay of the fast component becomes apparently enhanced (inset "b" of Figure 5) in the presence of oxygen. At no wavelengths, however, is seen an initial formation process, conformable to the initial fast decay, that can be attributed to the ring opening of I to II or equilibration to a mixture of I and II (following ET-sensitized formation of $S^{+\cdot}$ as I). This, however, does not rule out that II cannot coexist in small concentrations in equilibrium with I. In fact, the initial fast decay could be due to the equilibration of I to I + II. Upon steady-state photolyses under ET-sensitization by DCN, **11** undergoes epimerization to its meso form in both the absence and presence of oxygen. This result requires that the ring-opening of the radical cation from **11** has to occur. It is unlikely that the transient absorption observed under laser flash photolysis has a significant contribution from the open-ring, diradical species (III) formed by back ET in the ion pair because, first, such a species is not expected to enjoy a prolonged lifetime and, second, the extinction coefficients estimated at the end-of-pulse stage for $S^{+\cdot}$ at 640 nm (relative to DCN^-) agree well with those obtained from the spectra reported[17c,d] for the biphenyl radical cation.



I



II



II

The fractions (δ_T) of quenching events that result in DCN triplet formation (Table I) are small but non-negligible. In some cases, e.g., substrates **1**, **2**, **7–9**, and **11**, δ_T's are comparable to the intrinsic triplet yield ($\phi_T{}^0$) of DCN in acetonitrile (0.19).[10] Except with **10**, DCN triplet is not quenched by the substrates under study by energy or electron transfer. In photoreactions in the presence of O_2, the quenching of the DCN triplet should result in generation of singlet oxygen, a potential oxidant in addition to ground-state oxygen, and superoxide anion. The latter is formed by ET from DCN^- to O_2, a process that is exothermic by ~18 kcal/mol.[18]

Discussion

The principal finding in the present study is the spectacular yield of arylmethyl-type radicals as a result of fast, ET-initiated C–C bond cleavage in aryl-substituted pinacols (**1–3**) and pinacol ethers (**4** and **5**) and the cycloheptatrienyl derivative (**10**). The radical cations of these substrates are short lived ($\tau \leq$ 10 ns), as shown by the absence of a slow growth following laser flash at the absorption maxima of radicals. The lack of molar equivalence between DCN^- and substrate-derived radical, that is, $\delta_{anion} < \delta_{R\cdot}$, points to the production of a pair of the latter via back ET in the photogenerated radical ion pair, $DCN^{-\cdot}\cdots S^{+\cdot}$, followed by its dissociation from the solvent cage. That this back-donation also leads to the regeneration of the reactants, ^{1}DCN and S, is suggested by the sum total of ET-related yields, i.e., δ_{anion}, $^1/_2(\delta_{R\cdot} - \delta_{anion})$ and δ_T, being less than unity (except in the case of benzopinacol ether, **4**). In the case of tetraphenylethane, the radical cation ($S^{+\cdot}$) is longer lived (τ = 160 ns) and its dissociation, presumably via intramolecular ET from the C–C bond to initially produced radical-cation center localized on a phenyl group, occurs following its escape from the solvent cage. This mechanism is justified by the near-equivalence of $\delta_{R\cdot}$ and δ_{anion}.

A close scrutiny of the yield data for pinacols and pinacol ethers (Table I) reveals two trends. First, the efficiency of ET as manifested in δ_{anion} and $\delta_{R\cdot}$ is much larger for pinacol ethers than for pinacols. For benzopinacol ether, the net ET yield, $^1/_2(\delta_{anion} + \delta_{R\cdot})$, is quantitative. It is possible that specific hydrogen bonding, –CN···HO–, between pinacols and DCN in the association complex results in an orientation unfavorable for ET. More importantly, similar hydrogen bonding in the ET-derived ion pair or an intramolecular one (–OH··HO–) in $S^{+\cdot}$ may render nondissociative back ET facile. It is also plausible that the steric interaction within the radical pair derived from the ether is relatively severe and this facilitates their dissociation from the cage. Second, benzopinacol (**1**) and its ether (**4**) have much higher δ_{anion} and $\delta_{R\cdot}$ values than the corresponding acetophenone analogues (**2**, **3**, and **5**). Again, larger steric effects in the diaryl-substituted radical pairs, lower C–C bond energy, and greater stabilization of their radical and carbocationic fragments appear to be responsible for this trend. The steric factor also appears to contribute to high δ_{anion} in the case of tetraphenylethane (**9**).

Among the three bibenzyls (**6–8**) studied, the $K_{SV}{}^F$ data (Table I) correlate well with quencher oxidation potentials, the latter being dictated by methyl and methoxy substitution on phenyl rings. δ_{anion}'s are relatively high in these cases and, interestingly, follow a trend opposite to that of $K_{SV}{}^F$'s. The efficiency of back ET in the ion pair, measured in terms of $(1 - \delta_{anion})$ in these cases, decreases on going from **6** to **7** to **8**, that is, in a direction opposite to that of exothermicity of the process. Such an inverse relationship has also been observed[13] for a related series of quenchers, namely, methylated and methoxylated benzenes, for the DCN singlet.

Steady-state photochemical studies of bibenzyls **6** and **8** under photosensitization by DCN in oxygenated acetonitrile show that oxidative cleavage of the C–C bond occurs producing *p*-anisaldehyde and *p*-tolualdehyde in high yields (60–80%). Our laser flash photolysis data do not point to any appreciable formation of arylmethyl radicals (p-X-C_6H_4-$\dot{C}H_2$, X = OCH_3, CH_3) as a result of the fragmentation of the C–C bond in $S^{+\cdot}$. That the latter process does not take place is also indicated by the absence of **6** or **8** in photolysates following steady-state irradiation under deaerated conditions with **7** as donor, and of **7** in photolysates with **6** and **8** together as the donors.[5] Mechanisms different from those

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[16] Under energy-transfer sensitization by thioxanthone, **10** gives a transient spectrum at 300–330 nm that is superimposable on the spectrum of $Ph_2\dot{C}H$.

[17] (a) Sehested, K.; Hart, E. J. *J. Phys. Chem.* **1975**, *79*, 1639–1642. (b) Arai, S.; Veda, H.; Firestone, R. F.; Dorfman, L. M. *J. Chem. Phys.* **1969**, *50*, 1072. (c) Rodgers, M. A. J. *Trans. Faraday Soc.* **1971**, *67*, 1029–1040. (d) Das, P. K. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1135–1145.

[18] Based on redox potentials available in ref 4d and 4f.

based on oxygen attack on arylmethyl radical fragments (as evidenced in the case of substrates **1–5** and **9–11**) may be operative in the case of the bibenzyls, but these are yet to be worked out.

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Registry No. 1, 464-72-2; **2**, 4217-65-6; **3**, 22985-90-6; **4**, 985-93-3; **5**, 41047-48-7; **6**, 1657-55-2; **7**, 36707-23-0; **8**, 538-39-6; **9**, 632-50-8; **10**, 51990-81-9; **11**, 89986-86-7; DCN, 3029-30-9.

Hypermetalation Involving Sodium: ONa_3, ONa_4, $HONa_2$, and $HONa_3$[1]

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Abstract: In contrast to stoichiometries expected on the basis of the octet rule, but in agreement with experimental observations, ONa_3 (**1**, D_{3h}) and ONa_4 (**2**, T_d) are found by ab initio theory to be highly stable as isolated molecules toward all possible dissociation reactions, e.g., loss of a sodium atom or an Na_2 molecule. The calculated Na–O bond lengths are only slightly longer than those in Na_2O and NaOH. $HONa_2$ (**3**) and $HONa_3$ (**4**) provide further examples of hypermetalation. The ninth and tenth valence electrons in these effectively hypervalent molecules, **1–4**, are involved in metal–metal rather than in oxygen–metal bonding. The central oxygen atoms are content with the usual complement of electrons and do not have an expanded valence shell. Hypermetalation is predicted to be a very general phenomenon involving all the alkali metals in combination with many if not most of the other elements in the periodic table.

"Hypermetalated" molecules violate stoichiometries based on the octet rule.[1-3] Stimulated by the experimental observation of OLi_3 in the gas phase,[4] we examined not only this species, but also OLi_4, OLi_5, OLi_6, and a large number of analogous molecules calculationally.[1,2] These effectively hypervalent molecules are comprised of a first-row central atom and a "hyperstoichiometric" number of lithium substituents, e.g., FLi_3, NLi_5, CLi_6,[3] BLi_5, and $BeLi_6$.[1] As isolated entities, all are indicated to be highly stable thermodynamically toward all possible dissociation modes. Following our predictions, OLi_4 and OLi_5 were observed experimentally.[5] We now report that sodium can function in the same way as lithium. There are experimental precedents for similar hypermetalated species involving the heavier alkali metals, e.g., the "curious suboxides"[6] O_2Rb_9 and O_3Cs_{11} for which X-ray crystal structures are available.[7] During the course of our work on ONa_3 (**1**)[8] and ONa_4 (**2**),[1] their experimental detection in the gas phase was reported.[8] Ionization potentials were determined as well as similar measurements on K_3O and K_4O. However, neither geometries nor bonding information is available from experimental sources. This paper reports a calculational investigation of the sodium oxides, Na_nO (n = 1–4), as well as $HONa_2$ (**3**) and $HONa_3$ (**4**) and a number of related species. Comparisons are made with the closely related lithium molecules, e.g., OLi_3, OLi_4, and $HOLi_2$.

Computational Methods and Comments on Technical Details

Ab initio molecular orbital calculations were carried out with restricted and unrestricted Hartree–Fock theory using the GAUSSIAN 76[9] and 82[10] series of programs. The VAX version of the latter was adapted to the Erlangen CYBER 173 computer by Dr. A. Sawaryn. The structures of all molecules were optimized within the indicated point group using analytical force evaluation routines[11] and the 3-21G split valence basis set.[12] Improved energies were obtained from higher level single point calculations employing the polarization 6-31G* basis set which includes six d functions on all nonhydrogen atoms.[13] Valence electron correlation corrections were obtained for the smaller species with second-order (MP2) Møller–Plesset perburbation theory.[14] These results are designated 6-31G*//3-21G and MP2/6-31G*//3-21G, respectively.

A technical problem arose with the geometry optimization of ONa_3. With the small 3-21G basis set, the UHF wave function was spin contaminated; this increased with T-shaped C_{2v} distortion from D_{3h} symmetry ($\langle S^2 \rangle$ = 0.845 at D_{3h} and 1.592 at C_{2v}) and the energy was lowered artificially. Single point calculations at 6-31G* on the C_{2v} and D_{3h} 3-21G ONa_3 geometries indicated the latter to be lower in energy. Spin contamination was minimal ($\langle S^2 \rangle$ = 0.795 at C_{2v} and 0.782 at D_{3h}). Hence, we only report details for D_{3h} ONa_3 (**1**) here, but do not exclude the possibility of small C_{2v} distortions (as reported for OLi_3)[2,15]

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(1) For a preliminary account of this work and a review of related results, see: Schleyer, P. v. R. "New Horizons in Quantum Chemistry"; Löwdin, P.-O, Pullman, B., Eds.; Reidel: Dordrecht, 1983; pp 95–107. This is the third paper in a series on effectively hypervalent molecules; for parts 1 and 2, see ref 2 and 3, respectively.

(2) Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5839–5841.

(3) Schleyer, P. v. R.; Würthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5930–5932.

(4) Wu, C. H.; Kudo, H.; Ihle, H. R. *J. Chem. Phys.* **1979**, *70*, 1815–1820.

(5) Wu, C. H., private communication.

(6) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 254.

(7) Simon, A. *Struct. Bonding* (*Berlin*) **1979**, *36*, 81.

(8) Peterson, K. I.; Dao, P. D.; Castelman, A. W. Abstracts, 183nd National Meeting of the American Chemical Society, Las Vegas, Nev. *April* 1982; American Chemical Society, Washington, D.C., 1982; *J. Chem. Phys.*, **1984**, *80*, 563–564. Also see: Petersen, K. I.; Dao, P. D.; Castelman, A. W., Jr. *Ibid.*, **1983**, *79*, 777–783.

(9) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *11*, 368.

(10) Gaussian 82. Release A: Binkley, J. S.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, G.; Frisch, M. J.; Seeger, R.; Pople, J. A., Carnegie-Mellon University. The Erlangen group thanks Professor Pople for making a preliminary VAX version of this program available.

(11) Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632.

(12) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797–2803.

(13) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(14) Binkley, J. S.; Pople, J. A. *Int. J. Quantum. Chem.* **1975**, *9*, 229. Frisch, M. J.; Krishnan, R.; Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66, and references therein.