MS902 mass spectrometer. Support of the Purdue effort by the National Science Foundation is gratefully acknowledged.

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A Facile Diazenium Cation–Hydrazyl Radical–Nitroxide Radical Equilibrium. The Significance of Charge-Transfer Intermediates

Sir:

The dynamics of the diazenium cation–hydrazyl radical equilibrium and associated redox and proton-transfer equilibria have been the subject of intense investigation recently.[1,2] The studies have succeeded largely as a consequence of the successful preparation of a series of stable trialkyl diazenium salts.[2] In the present report, we disclose a new synthetic entry to this compound class, the occurrence of easily detected charge-transfer complexes, and the significance of C-T interactions for the diazenium cation–hydrazyl radical equilibrium. In addition, the generation of the first 1,2-dialkyl-2-arylhydrazyl radical, a species in equilibrium with a cyclic nitroxide radical, is described.

Table I. Ultraviolet and Visible Absorption Maxima as a Function of Solvent for the *tert*-Butyldiazenium Salts **2**$^+$ and the 2,4-Dinitrophenyldiazenium Bromide **4**$^+$ (λ_{max}, nm ($\epsilon_{apparent}$, M^{-1} cm^{-1})[a,b]

	H_2O	CH_3OH	CH_3CN	CH_2Cl_2
$2^+ClO_4^-$	311 (99)	311 (96)	311 (100)	312 (100)
2^+Cl^-–3	310 (100)	311 (110)	310 (100)	300 (195)[c]
2^+Br^-–3	310 (99)	311 (100)	310 (130) 350 (25) sh	308 (220) 346 (160) sh
2^+I^-–3	310 (110) 350–600 (<10)[d]	311 (120) 360 (30) sh	311 (120) 404 (30)	310 (190) 436 (380)
$4^+ClO_4^-$	284 (6500)	285 (6400) sh	286 (7400)	291 (6000)
4^+Br^-–7	280 (6700) sh	285 (6200) sh	285 (6600) 425 (105)[e] sh	288 (6900) 458 (370)[f]

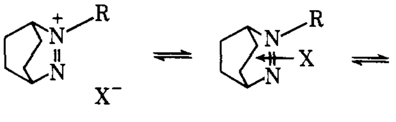
[a] Calculated from the observed optical density and the initial concentration. Except were noted, the latter was 1.0×10^{-2} M for all **2**$^+$ salts and 1.0×10^{-4} M for **4**$^+X^-$. [b] All of the substances listed likewise show high intensity absorption <230 nm. [c] This band is significantly broader than the corresponding peak for $2^+ClO_4^-$. [d] A long tail with no distinct λ_{max}. [e] 1.0×10^{-2} M. [f] 1.0×10^{-3} M.

Treatment of 2,3-diazabicyclo [2.2.2]oct-2-ene (DBO)[3] with 1 equiv of $HClO_4$ (Et_2O, 25°) leads to the stable protio-diazenium cation **1**$^+ClO_4^-$ (mp 210–212°, 87%).[4] The latter is smoothly converted to the *tert*-butyl salt **2**$^+ClO_4^-$ (mp 242–243°, 90%) upon refluxing in *tert*-butyl alcohol.[5] Alternative counterions are obtained by ion exchange (**2**$^+$, Bio-Rad AG MP-1: Cl^-, mp 191–192°, 79%; Br^-, mp 226–227°, 88%; NaI-CH_2Cl_2: I^-, mp 223–224°, 91%).

Table I displays the uv-visible absorption maxima for the series **2**$^+$. In strongly ionizing solvents (H_2O, CH_3OH), each salt exhibits a weak band at 310 nm (ϵ 100–120 M^{-1} cm^{-1}) attributed to the diazenium moiety. As the solvent polarity is reduced, an additional band which does not obey Beer's law appears at longer wavelengths. The magnitude of the effect descends in the following order, X: I > Br > Cl. The influence of the solvent on the uv-visible spectra, the relative ionization potentials of the gegenions,[6] and the position of the new absorption maxima permit assignment of the latter to the long-wavelength charge-transfer band[7-9] of complex **3**.

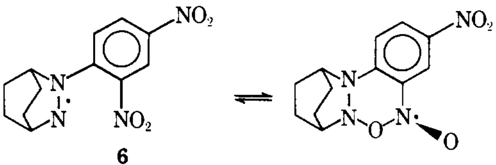
Suitable modification of the heterocyclic acceptor moiety which leads to a decrease in the energy of the lowest unoccupied molecular orbital,[7c,9] can be expected to lead to a magnification of the acceptor properties of **2**$^+$. Charge transfer might then proceed to complete electron transfer. Accordingly, treatment of DBO with 2,4-dinitrobromobenzene (Et_2O, 25°) occurs cleanly to give the phenylated system **4**$^+Br^-$ (mp 152–153°, 83%). Exchange of the bromide ion ($NaClO_4$-H_2O) furnishes **4**$^+ClO_4^-$ (mp 179–180°). Analogous to the *tert*-butyl salts **2**$^+$, compound **4**$^+Br^-$ exhibits charge-transfer behavior in the uv-visible with broad low energy absorption at 458 nm in CH_2Cl_2, whereas the perchlorate salt is transparent in this region (Table I). Halide exchange (NaI-H_2O) yields **4**$^+I^-$ (mp 119–120°, 73%) a purple diamagnetic solid (Gouy balance determination). On the contrary, dissolution of the latter in CH_2Cl_2, halide exchange of **4**$^+Br^-$ in organic media (NaI-CH_2Cl_2), or direct alkylation of DBO with 2,4-dinitroiodobenzene (Et_2O or C_6H_6, reflux) yields a green paramagnetic solution (λ_{max}(CH_2Cl_2) 690 nm (ϵ 6500 M^{-1} cm^{-1})) with an ESR spectrum of three lines of equal intensity ($g = 2.0038$, $a_N = 12.2$ G, C_6H_6). Further resolution into about 40 lines could be achieved by degassing, but the hyperfine couplings were not assigned. The solution is stable to oxygen for 9–12 hr. No other radical is evident after the original ESR signal disappears, in contrast to observations for trialkyl hydrazyl radicals.[2b] The same paramagnetic species is generated by the action of PbO_2 on the corresponding hydrazine, *N*-(2,4-dinitrophenyl)-2,3-diazabicyclo[2.2.2]octane (**5**).[10] Intuitively, hydrazyl radical **6** is the product expected from these reactions.

At first glance, the three-line spectrum and the *g* value appear inconsistent. All hydrazyl radicals so far studied[11] show five-line spectra as a result of coupling with both nitrogens ($a_{N_1} \cong a_{N_2} = 10$-$12$ G, $g = 2.0030$-2.0040). However, the ortho nitrophenyl group of **6** can act as an internal spin trap[12] to produce the nitroxide radical **8**. The unusually low *g* value can be accommodated by recognizing that *g* values of nitroxide radicals decrease upon phenyl substitution,[13] ring formation,[12a,c] and with increasing electron release by substituents.[14] Structure **8** incorporates all of these features and possibly enhances their combined effect by the near planarity of the tetraheterocyclic ring.



$X^- = ClO_4^-, Cl^-, Br^-, I^-$

	R		R
1^+	H	**3**	*tert*-butyl
$\mathbf{2}^+$	*tert*-butyl	**7**	2, 4-DNP
$\mathbf{4}^+$	2, 4-DNP		



6 **8**

Further evidence regarding the nature of the paramagnetic species was gathered by electrochemical reduction of cation $\mathbf{4}^+Br^-$. Cyclic voltammetry (CH_2Cl_2) shows two consecutive reversible one-electron redox couples with radical and anion peak potentials at $E^1{}_{p/2} = +0.21$ and $E^2{}_{p/2} = -0.65$ V respectively (vs. SCE). Coulometric reduction of $\mathbf{4}^+Br^-$ at +0.21 V (CH_2Cl_2, argon) leads to a green solution identical in all respects (uv-visible, ESR) with the chemically generated radical. A cyclic voltammogram of the latter solution is superimposable with that obtained from $\mathbf{4}^+Br^-$ assuring that the species showing reversible electron transfer at +0.21 V corresponds to that on which ESR and uv-visible measurements have been made. We conclude therefore that the green paramagnetic species possesses the cyclic structure **8**.

The electrochemical measurements establish a rapidly attained equilibrium between radicals **6** and **8**. The additional participation of cation $\mathbf{4}^+$ in the equilibrium is shown by visible spectroscopy. A 5.0×10^{-4} *M* solution of $\mathbf{4}^+Br^-$ (CH_3CN) when treated with varying quantities of sodium iodide and monitored at 690 nm immediately evidences radical **8**. The relationship between [NaI] and [**8**] is smooth but nonlinear as expected for the partition between $\mathbf{4}^+I^-$ and **8**. In addition to the latter, I_3^- ($\lambda_{max}(CH_3CN)$ 368 nm) is likewise generated by the introduction of iodide. Attempts to define the stoichiometry of the equilibrium by considering both the electrochemical and the visible data have not yet been successful. The penultimate system is undoubtedly complex and probably involves additional species such as I_5^- and I_7^-.

In summary the diazenium cation moiety behaves as both a partial and a full[2] charge acceptor depending on its substituent pattern and the structure of the donor. Although the uv-visible spectrum of the I_3^- ($\epsilon \sim 26{,}000$ M^{-1} cm^{-1} [16]) and nitroxide **8** mixture prevents direct observation of a weakly absorbing charge-transfer complex, the results of Table I make it probable that one of the nonradical components of the system is in fact such a species, i.e., **7**. Full electron transfer is promoted easily and reversibly by the simple expedient of adding excess iodide ion. In the present case, the equilibrium is shifted still further by ring closure of hydrazyl **6** to the stable nitroxide **8**.[17] We are investigating the properties of **6**/**8** and related systems further.

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(10) Phenylhydrazine (**5**) was synthesized by alkylation of 2,3-diazabicyclo[2.2.2]octane[3] with 2,4-dinitrochlorobenzene ($EtOH$–$NaHCO_3$–N_2, 25°, 24 hr, mp 170–171°, 70%).

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(18) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1971–1976.

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Benzoyl Cations. The Correlation of Thermodynamic Stabilities and ^{13}C Nuclear Magnetic Resonance Chemical Shifts with Hammett σ Values and CNDO/2 Charge Densities

Sir:

Recently there has arisen a controversy over the extent to which ^{13}C chemical shifts can be used as a measure of the charge distribution in stable carbocations in superacid media.[1,2] Due to the extensive use of ^{13}C chemical shifts as an indication of charge distribution in carbocations, this is an important issue. We have measured relative thermodynamic stabilities and carried out CNDO/2 calculations on a series of substituted benzoyl cations for which ^{13}C NMR chemical shifts are available.[3,4] While the thermodynamic stabilities correlate nicely with Hammett σ values, the ^{13}C chemical shifts do not. The acyl carbon ^{13}C chemical shift shows a rather scattered but obvious linear correlation with the CNDO/2 charge density. Correlations having a *negative* slope are observed between calculated charge densities and ^{13}C chemical shifts of the ring carbons.

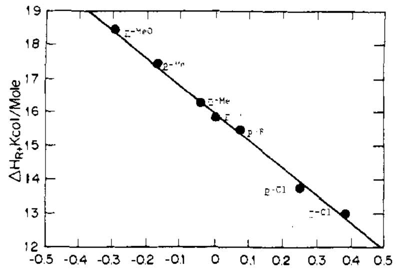

Figure 1.

The relative heats of formation (ΔH_{R+}) of a series of benzoyl cations in 11.5 mol % antimony pentafluoride-fluorosulfonic acid at 25° are plotted vs. σ in Figure 1. The relative heats of formation are, as before,[5-7] heats of transfer of the precursor from dilute solution in carbon tetrachloride to dilute solution in the superacid and give accurate values for the substituent effect on the enthalpy required to convert the covalent precursor into the cation. All ions are quite stable and are formed cleanly, as verified by NMR work both in our laboratories and others.[3] The excellent straight line obtained when ΔH_{R+} is plotted against σ indicates that the normal Hammett σ values are quite appropriate for use in the superacid medium. There are no unusual solvent effects occurring which would make necessary the use of another set of substituent parameters. A correlation with σ rather than σ^+ is expected since, in both the ground state molecule and the ions, the substituents and the reaction center are directly conjugated.[8] The relative heats of formation reported here also give a good correlation with the solvolysis rates for some of the same benzoyl chlorides in aqueous formic acid.[9] When the ^{13}C chemical shifts are plotted vs. σ, no correlation is observed. A very general trend is observed when σ^+ is used, but the correlation is still very poor. This absence of a correlation of δ ^{13}C with σ contrasts with previously observed correlations of δ ^{13}C with σ in di- and triphenyl methyl cations.[10,11]

Table I contains the ^{13}C chemical shifts together with charge densities calculated using Pople's CNDO/2 technique.[12] Standard geometries were used and the charge densities calculated using the standard and X-ray geometries for the *p*-methylbenzoylium ion were quite similar, as shown.[13] The ring-C_α bond length used was 1.387 Å and the -C=O bond length adopted was 1.111 Å, based on X-ray data.[14] The C-Cl bond length used was 1.70 Å. In row 9 of the table, the equation for the least-squares plot of charge density vs. δ ^{13}C is reported. The acyl carbon shows a linear plot, correlation coefficient 0.908, with a slope of 629 ppm/electron. This is a much greater slope than that usually reported, ca. 160 ppm/electron.[15,16] Furthermore, the ring carbons all give negative slopes when σ is plotted against the charge density. Thus different carbon atoms in the same molecule give different slopes when their δ ^{13}C is plotted vs. charge density. The problem does not seem to lie in the geometry used for the CNDO/2 calculations. As shown in Table I and as expected for the parameterization of the CNDO/2 method, the calculated charge densities are not very sensitive to small changes in geometry. The results for the *p*-methylbenzoylium ion are quite similar using the X-ray geometry, which shows significant ring distortion, and Pople's standard geometry. However, it is quite possible that these calculations are not giving accurate charge densi-

Table I. Carbon-13 Chemical Shifts,[a] Calculated Charge Densities,[b] and Their Least-Squares Correlation in Substituted Benzoyl Cations

X	C_α		C_1		C_2		C_3		C_4		Other shifts and charge densities
	δ	Charge	δ	Charge	δ	Charge	δ	Charge	δ	Charge	
H	38.9	0.5004	106.0	−0.0330	52.4	0.0881	60.8	0.0063	44.3	0.0876	
p-CH_3 (std)	37.2	0.4891	110.9	−0.0525	53.4	0.0912	60.2	−0.0170	27.4	0.1339	CH_3, 169.2, −0.0407
p-CH_3 (X-ray)		0.4797		−0.0628		0.0922		−0.0261		0.1551	CH_3, −0.0769
p-F	39.1	0.4990	110.3	−0.0494	48.3	0.1069	71.8	−0.0496	18.0	0.3208	
p-Cl	37.6	0.4991	106.6	−0.0324	47.8	0.0884	55.7	0.0093	32.8	0.1432	
p-CH_3O–	32.3	0.4917	116.6	−0.0608	48.9	0.1060[c]	73.5	−0.0685[d]	17.3	0.2703	CH_3O, 133.9, −0.1731
m-CH_3–	37.0	0.4929	105.4	−0.0325	52.5	0.0590	47.8	−0.0556	41.7	0.0655	C_5, 60.8, 0.0131 C_6, 53.5, 0.0735
p-C=O^+	48.5	0.5150	85.3	0.0351	52.1	0.0815					
Correlation line, CD =	0.00159δ + 0.437		−0.00320δ + 0.307		−0.00402δ + 0.293		−0.00448δ + 0.266		−0.00827δ + 0.420		
Correlation coefficient	0.908		0.994		0.580		0.976		0.928		

[a] Measured in SbF_5 at 20°, in ppm from $^{13}CS_2$ ($\delta_{TMS}{}^{CS_2}$ 193.7), from ref 3. [b] CNDO/2, standard bond lengths and angles used. [c] Average of syn and anti (to O–CH_3). [d] Syn to O–CH_3, anti −0.0534.