solutions but lacking the alkene. The combined ether extracts were analyzed by GLC. All of the epoxides and diols were known compounds, and their IR, 300- or 400-MHz ^{1}H NMR, and 75.4-MHz ^{13}C NMR spectral data[25] were identical with those given in the literature or with those of commercial samples.

Control Experiments on Stability of $KHSO_5$. Iodometric titrations of reaction mixtures immediately after epoxidations of cyclohexene and of cyclooctene at initial pH 1.58 and of cyclohexene at initial pH 6.75 showed that all of the excess oxidant remained after 5 h of reaction under acidic conditions and all of the excess oxidant disappeared after 5 h of reaction under neutral conditions.

Acknowledgment. We thank the U.S. Army Reserach Office for support of this research.

Registry No. $PhC(CH_3)(OH)CH_2OH$, 4217-66-7; $PhCH(OH)CH_2OH$, 93-56-1; p-$MeC_6H_4CH(OH)CH_2OH$, 13603-62-8; $PhCH_2CH(OH)CH_2OH$, 17131-14-5; oxone, 37222-66-5; 2,3-dimethyl-2-butene, 563-79-1; 1-methylcyclohexene, 591-49-1; cyclohexene, 110-83-8; α-methylstyrene, 98-83-9; *cis*-β-methylstyrene, 766-90-5; *trans*-β-methylstyrene, 873-66-5; styrene, 100-42-5; tetrachloroethylene, 127-18-4; p-methylstyrene, 622-97-9; cyclooctene, 931-88-4; allylbenzene, 300-57-2; 1-octene, 111-66-0; 2,3-dimethyl-2,3-butanediol, 76-09-5; 1-methyl-1,2-cyclohexanediol, 6296-84-0; *trans*-1,2-cyclohexanediol, 1460-57-7; *erythro*-1-phenyl-1,2-propanediol, 1075-04-3; *threo*-1-phenyl-1,2-propanediol, 1075-05-4; tetramethyloxirane, 5076-20-0; 1-methylbicyclo[4.1.0]heptane, 2439-79-4; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 2-methyl-2-phenyloxirane, 2085-88-3; 2-methyl-3-phenyloxirane, 4436-22-0; phenyloxirane, 96-09-3.

Gas-Phase Reactivities and Interchromophoric Effects in 1,*n*-Dicarbazolylalkane Cations and Related Species†

Steven M. Schildcrout,*‡ Randolph B. Krafcik,§ and John Masnovi*§

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115, and Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555

Received November 27, 1990

The behavior of gaseous cations derived from electron ionization (20 and 70 eV) and methane chemical ionization (CI) of 1,*n*-dicarbazolylalkanes **1a–5a** (where n = 1–5 methylene units, respectively) and the corresponding 3-nitro derivatives **1b–5b** was examined using mass spectrometry. An iminium ion (m/z 180) is the major fragment from all **1–5** examined with the exception of **4a**, for which CI affords predominantly a pyrrolidinium ion (m/z 222) by displacement of carbazole. Compounds **1a** and **1b** exhibit little $[M]^{\cdot+}$ and $[M + H]^+$ and undergo the most extensive fragmentation. Ethylated iminium ion (m/z 208) is observed from both **1a** and **1b** under CI conditions, indicating operation of an interannular hydrogen shift. Compound **3a** fragments least, consistent with an exceptional, although small, stabilization for the parent ions of this derivative.

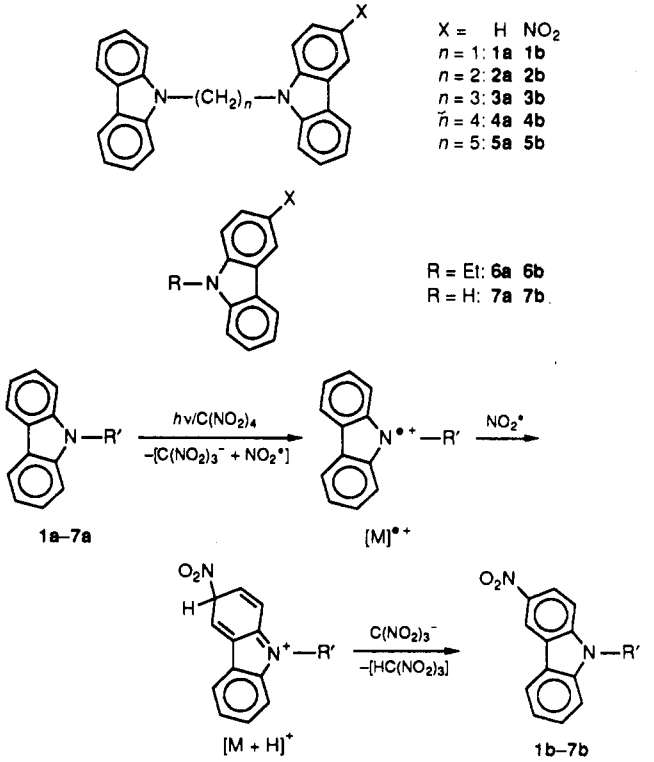
Introduction

The interaction of aromatic rings is one of a number of intermolecular attractive forces[1-7] which can influence molecular structure[5-7] and determine the course of chemical reactions.[8,9] Evidence has been presented for stabilization of arene dimers with stacked[10,11] and "T-shaped"[12,13] configurations. Association is even more favorable for radical cations of aromatic hydrocarbons than for neutral arenes.[14,16] Aggregation affects chemical behavior; for example, radical cations of arene dimers react with nucleophiles and radical species significantly more slowly than do the corresponding monomers.[17,18]

In this regard, we have investigated the crystal structures and reactivities in solution of dicarbazolylalkanes **1–5** (Scheme I) in which two carbazole rings are linked at nitrogen by a polymethylene spacer of varying length.[7,18,19] The number of methylene carbons in these dicarbazole derivatives (being one to five for **1–5**, respectively) restricts the geometries for intramolecular interaction between the two terminal carbazole groups. Therefore, interchromophoric interactions can be seen as a function of the length of the saturated chain linking the carbazoles. The nature of such interactions, in turn, influences the delocalization of charge and spin upon oxidation of **1–5** to the respective radical cations $[M]^{\cdot+}$.[20]

Specifically, interaction between two carbazole rings was found to be stabilizing for $[M]^{\cdot+}$ of **3a**, in which "sandwich" or parallel planar overlap is possible (I) and charge is delocalized between both carbazole rings.[21] Only a small

Scheme I



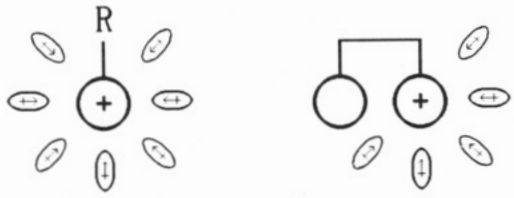
† Presented in part at the 201st National Meeting of the American Chemical Society, Atlanta, GA, 14–19 April, 1991.

‡ Youngstown State University.

§ Cleveland State University.

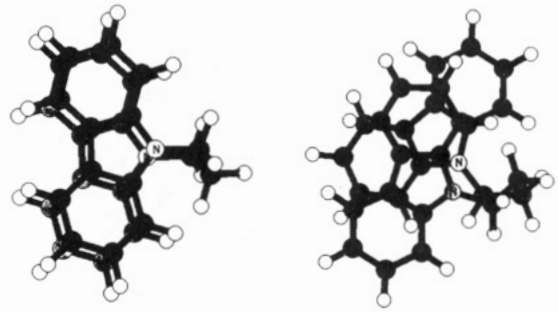
0022-3263/91/1956-7026$02.50/0

Scheme II

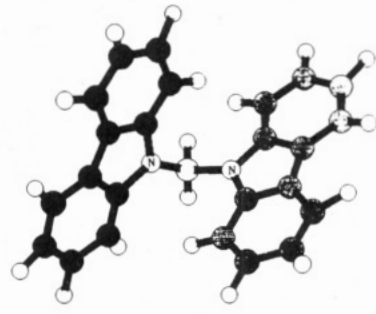


stabilization was observed for $[M]^{\bullet+}$ of **4a**, in which a "nonsandwich" parallel planar interaction (such as one with parallel planes but axes not aligned, II) is possible. No stabilization was evident for $[M]^{\bullet+}$ of **2a** and **5a**, for which only nonplanar interactions are accessible.[18] The carbazole groups of **1a** also are prohibited from being parallel, although they are constrained to lie close together (III). Interestingly, although $[M]^{\bullet+}$ of **1a** appears to have charge delocalized over both carbazole substituents, it is more reactive than $[M]^{\bullet+}$ of any other derivative, including *N*-ethylcarbazole (**6**).

Ion pairing and solvent effects can lead to pronounced changes in the behavior of radical and nonradical ions.[4,22] The presence of a second carbazole group near an ionized carbazole, for example, may lead to shielding of charge from solvent and counterions on one side of the ionic carbazole. Thus, reactivity may be modified even in the absence of direct electronic interactions between the two carbazole groups (Scheme II).



I II



III

In the present study, positive ion mass spectra were obtained for **1a–5a**, the unsymmetrical 3-nitro derivatives **1b–5b**, and four other related compounds using standard and reduced-energy electron ionization (EI) and methane chemical ionization (CI). This work was undertaken in order to deduce the underlying gaseous ion chemistry, including substituent and possible interchromophoric effects, in the absence of ion pairing and solvent or other matrix. Two simple monochromophoric systems, *N*-ethylcarbazole (**6a**) and carbazole (**7a**), have been included for comparison. The mononitro derivatives **1b–7b** also were examined, for the following two reasons. First, the nitro functionality strongly destabilizes positively charged systems. Furthermore, chemical ionization of **1b–5b** affords species related structurally to species generated in solution (the Wheland intermediates, Scheme I). The results of this study indicate that the reactivities of **1–5**, in terms of their unimolecular fragmentations, can address the type and extent of interactions between the carbazole substituents.

Experimental Section

Instrumentation. Proton and carbon NMR spectra were obtained in $CDCl_3$ (Cambridge Isotope) solution (Me_4Si internal reference) on a Bruker AC300F (300 MHz proton) spectrometer. Melting points were obtained on a Hoover Unimelt capillary melting point apparatus and are uncorrected. Mass spectra were obtained on a Finnigan MAT 1020B mass spectrometer with EI and CI ion sources and direct probe inlet. Analyses were performed at Desert Analytics.

Preparation of Compounds. Dicarbazolylalkanes **1a** and **3a–5a** were prepared from carbazole (Lancaster) and dibromomethane (Cationics Inc.), dibromopropane and dibromopentane (Aldrich), and dibromobutane (MCB), as described in the literature syntheses.[23] A modified synthesis of 1,2-dicarbazolylethane **2a** was followed. To carbazolyllithium prepared from equimolar amounts of carbazole and methyllithium in toluene was added ethylene glycol ditosylate,[24] and the mixture was heated at reflux

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for 20 h. Workup followed the literature procedure.[23]

Carbazole (Lancaster) (**7a**), *N*-ethylcarbazole (**6a**) (K & K), and dicarbazolylalkanes **1a–5a** were purified by chromatography on silica gel (Baker, ~40 μm for flash chromatography) or alumina (Woelm activity III) using fractional elution with dichloromethane–hexanes. Nitrocarbazole derivatives **1b–7b** were prepared by photochemical nitration of charge-transfer complexes of dicarbazolylalkanes **1a–7a** using a 50% molar excess of tetranitromethane in dichloromethane and a Corning glass 500-nm sharp cut-off filter.[18] Yields of **1b–5b**, based on 20–40% conversion of **1a–5a**, were essentially quantitative as determined by NMR analysis of crude reaction mixtures in $CDCl_3$ solvent. Purification of the nitrocarbazoles **1b–6b** was accomplished by chromatography on silica gel or Florisil (Fischer, 100–200 mesh) eluting fractionally with dichloromethane–hexane. Isolated yields of the mononitro compounds **1b** and **2b** in particular were very low due to difficulties in separation of unreacted **1a** or **2a** and lesser amounts of dinitrated analogues.

1b: ^{1}H NMR δ 9.00 (1 H, d, J = 2.4 Hz), 8.31 (1 H, m), 8.11 (3 H, m), 7.2–7.6 (10 H, m), 6.76 (2 H, s); yellow needles; mp 268–70 °C. Anal. Calcd for $C_{25}H_{17}N_3O_2$: C, 76.71; H, 4.38; N, 10.73. Found: C, 76.33; H, 4.30; N, 10.94.

2b: ^{1}H NMR δ 8.82 (1 H, d, J = 2.2 Hz), 8.07 (1 H, d, J = 7.4 Hz), 8.00 (1 H, dd, J = 2.3, 9.1 Hz), 7.96 (2 H, d, J = 7.2 Hz), 7.49 (1 H, td, J = 7.1, 1.1 Hz), 7.33 (2 H, td, J = 7.1, 1 Hz), 7.23 (2 H, dt, J = 8.2, 1.1 Hz), 7.13 (2 H, td, J = 7.5, 1.0 Hz), 6.94 (2 H, d, J = 8.1 Hz), 6.66 (1 H, d, J = 9.0 Hz) 4.78 (4 H, s); ^{13}C NMR δ 143.3, 141.1, 140.7, 139.8, 127.5, 125.8, 123.2, 123.1, 122.6, 121.4, 121.15, 121.12, 120.5, 119.5, 117.0, 108.8, 107.4, 107.3, 41.9, 41.3; yellow plates; mp 230–2 °C (from benzene).

3b: ^{1}H NMR δ 8.99 (1 H, d, J = 2.2 Hz), 8.25 (1 H, dd, J = 2.3, 9.0 Hz), 8.14 (3 H, m), 7.43 (3 H, m), 7.26 (5 H, m), 7.17 (1 H, d, J = 8.5 Hz), 7.02 (1 H, d, J = 9.1 Hz), 4.45 (2 H, t, J = 6.9 Hz), 4.31 (2 H, t, J = 7.6 Hz), 2.52 (2 H, quintet, J = 7.1 Hz); ^{13}C NMR δ 143.1, 141.2, 140.9, 140.2, 127.5, 126.0, 123.2, 122.9, 122.7, 121.7, 121.1, 121.0, 120.7, 119.4, 117.3, 109.3, 108.4, 107.9, 40.9, 40.3, 27.8; yellow needles; mp 227–30 °C. Anal. Calcd for $C_{27}H_{21}N_3O_2$: C, 77.31; H, 5.05; N, 10.02. Found: C, 77.04; H, 5.07; N, 9.76.

4b: ^{1}H NMR δ 8.98 (1 H, d, J = 2 Hz), 8.28 (1 H, d, J = 8.8 Hz), 8.12 (3 H, m), 7.37 (3 H, m), 7.27 (6 H, m), 7.12 (1 H, d, J = 9.3 Hz), 4.32 (2 H, t, J = 6.3 Hz), 4.17 (2 H, t, J = 6.3 Hz), 1.98 (4 H, m); ^{13}C NMR δ 143.2, 141.4, 140.7, 140.2, 127.4, 125.8, 123.0, 122.8, 122.6, 121.6, 121.0, 120.8, 120.5, 119.1, 117.3, 109.5, 108.5, 108.1, 43.2, 42.5, 26.6, 26.5; yellow needles; mp 221–3 °C. Anal. Calcd for $C_{28}H_{23}N_3O_2 \cdot {}^1/_2CH_2Cl_2$: C, 71.92; H, 5.08; N, 8.83. Found: C, 71.81; H, 5.05; N, 8.60.

5b: ^{1}H NMR δ 8.99 (1 H, d, J = 2.2 Hz), 8.29 (1 H, dd, J = 9.1 and 2.3 Hz), 8.12 (3 H, m), 7.53 (1 H, td, J = 7.7 and 1.2 Hz), 7.43 (2 H, td, J = 7.7 and 1.2 Hz), 7.20–7.35 (7 H, m), 4.26 (2 H, t, J = 6.8 Hz), 4.24 (2 H, t, J = 6.8 Hz), 1.89 (4 H, m), 1.41 (2 H, m); ^{13}C NMR δ 143.4, 141.5, 140.6, 140.3, 127.4, 125.7, 122.9, 122.5, 121.6, 121.0, 120.8, 120.4, 118.9, 117.3, 109.6, 108.4, 108.1, 43.3, 42.7, 28.83, 28.81, 25.25; yellow needles; mp 124–6 °C. Anal. Calcd for $C_{29}H_{25}N_3O_2$: C, 77.83; H, 5.63; N, 9.39. Found: C, 77.66; H, 5.65; N, 9.11.

The structures of **1a–5a** and **3b** have been confirmed by single-crystal X-ray structure determinations and will be reported separately.[7,18,25]

Mass Spectra. Acetone or dichloromethane solutions containing on the order of 1 μg of the compound were evaporated at room temperature or with gentle heating in Pyrex sample tubes. These were introduced into the mass spectrometer and ramped at 2 deg/s over a range depending on the volatility of the compound. The quadrupole mass analyzer, with an upper limit of m/z 800, was operated at unit resolution. It was tuned and calibrated daily with perfluorotributylamine (FC-43) and was used for repetitive full scans typically at 2 s/scan.

EI spectra were obtained at 70 and 20 eV. The CI reagent gas was ultrahigh-purity methane at 50 Pa. Spectrum averaging with background subtraction was carried out with the data system. To avoid interference from possible impurities, ions were further verified as arising from the same compound by the similarity of their single-mass intensity versus time profiles as the sample vaporized from the probe. Although previous work has shown that nitroarenes may undergo reduction to the amine under certain conditions in a CI ion source,[26,27] no ions (such as an apparent $[M + H - 30]^+$) attributable to such amines were detected in the CI spectra here. However, the CI spectra of **1b** and **2b** showed evidence of thermal reactions in the ion source leading to monocarbazolyl species. Ions from these species have been excluded from Table IV.

Chemical assignments of ions were verified whenever possible by agreement between observed and calculated natural isotopic abundances. Isotopic abundances were used also to calculate relative abundances for chemically different ions whose isotopic clusters overlap, as for $[M]^{\cdot+}$ and $[M + H]^+$ in the CI mode. Abundances are given as percent of the total ion abundance, rather than of the most abundant ion. This is advantageous in comparing spectra of related compounds.[28]

EI spectra at 70 eV have been reported for monochromophoric compounds **6a**, **6b**, **7a**, and **7b** only; neither energy variation in EI nor CI spectra have been reported.[29–31]

Results and Discussion

Electron-Transfer Nitration. Photochemical nitration of carbazole derivatives with tetranitromethane has been shown to proceed by the single electron transfer mechanism illustrated in Scheme I. Carbazole radical cations, $[M]^{\cdot+}$ for **1a–5a**, form in dichloromethane solution by charge-transfer excitation of electron donor–acceptor complexes with tetranitromethane. These radical cations react with $NO_2^{\cdot}$ formed by fragmentation of tetranitromethane radical anion to produce iminium ion intermediates, $[M + NO_2]^+$ for **1a–5a**. The corresponding 3-nitrocarbazole derivatives **1b–5b** and nitroform are produced essentially quantitatively.

Electron ionization of carbazoles **1a–5a** will produce the radical cations $[M]^{\cdot+}$ in the absence of solvent. Chemical ionization with CH_4 reagent gas produces predominantly the even-electron cations $[M + H]^+$ and cations from alkylation (mostly $[M + C_2H_5]^+$) for **1a–5a**, in addition to varying amounts of radical cations $[M]^{\cdot+}$. Thus, proton-transfer CI of the nitrocarbazoles **1b–5b** would be expected to characterize primarily the cations $[M + H]^+$ of **1b–5b**, which will be the same as (or isomeric with) the iminium ion intermediates $[M + NO_2]^+$ produced from **1a–5a** in the nitration reaction of Scheme I. Determination of fragment ions of **1b–5b** will indicate the preferences with respect to the ring, nitrated or unnitrated, on which positive charge preferentially will reside.

Gas-Phase Electron Ionization of Dicarbazolylalkanes. Relative abundances of ions resulting from 70 eV EI are shown in Table I for **1a–7a**. Only the principal ions are shown, with isotope peaks excluded. For example, the abundance at m/z 181 for **3a** is from $[C_{13}H_{11}N]^{\cdot+}$ and does not include the ^{13}C contribution from $[C_{13}H_{10}N]^+$. The present results for **6a** and **7a** agree with those previously reported,[29] including a study of **7a** giving meta-

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Table I. Relative Abundances of Carbazolylalkane Ions as Percent of Total[a] (EI at 70 eV)

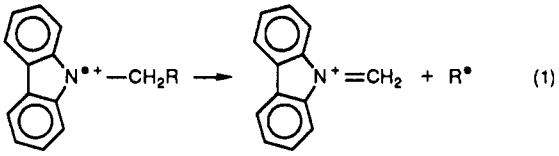
ion	1a	2a	3a	4a	5a	6a	7a
$[M]^{\bullet+}$	6.9[b]	9.2[b]	16.3[b]	13.6[b]	15.7[b]	27.6[b]	58.0[b]
	(346)	(360)	(374)	(388)	(402)	(195)	(167)
$[M]^{2+}$	2.4	–[c]	3.3	3.8	2.5	2.3	10.0
	(173)	(180)	(187)	(194)	(201)	(97.5)	(83.5)
$[M - H]^+$	0.1				0.1	1.3	12.6
	(345)				(401)	(194)	(166)
$[M - 166]^+$	–[c]		0.2	2.8[b]	0.2		
	(180)		(208)	(222)	(236)		
$[M - 167]^{\bullet+}$	1.1	0.8	1.1[b]		1.1[b]		
	(179)	(193)	(207)		(235)		
m/z 206			7.2	0.6	0.6		
m/z 181			2.6[b]				
m/z 180	63.7	59.7	46.4	57.7	57.7	47.0	
m/z 166	1.5	0.6	1.9	1.5	1.8	2.1	–[d]
m/z 152	9.4	8.3	7.4	6.9	6.6	6.6	0.1

[a] Only principal ions are tabulated; isotope peaks are excluded (m/z values in parentheses). [b] These abundances increase at 20 eV. [c] See m/z 180. [d] See $[M - H]^+$.

stable processes and a comparison with 1,8-dideuteriocarbazole.[30]

Table I indicates those ions whose relative abundances are greater at 20 eV than at 70 eV. These ions include each $[M]^{\bullet+}$ as well as fragments formed via low-energy paths such as rearrangement. Low-energy abundances are not tabulated because fragmentation at 20 eV increased with probe temperature, making quantitative comparisons among the compounds less meaningful than at 70 eV. This effectiveness of thermal energy in ion decomposition at low ionizing energies agrees with statistical theory.[32]

Ionization energies for a series of carbazole derivatives containing a single carbazole ring were reported to be lower and less varied than those of the comparable aromatic hydrocarbons,[33] implying that the radical-charge site in $[M]^{\bullet+}$ for carbazoles heavily involves the nitrogen atom. Comparing **1a–7a**, the most abundant $[M]^{\bullet+}$ and $[M]^{2+}$ are shown by **7a**, whose fragmentation opportunities are limited mainly to $H^{\bullet}$ loss. Spectra of the other compounds, however, are dominated by similarly high abundances of $[C_{13}H_{10}N]^+$ at m/z 180 with a conjugated iminium structure resulting from facile α-homolytic cleavage, which is typical of amines (eq 1).[34] Among these seven compounds,



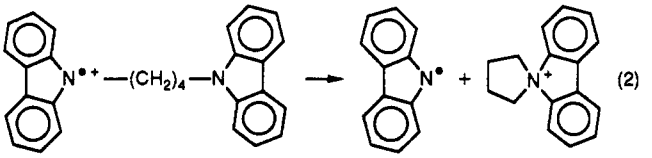
(1)

m/z 180

1a shows the greatest relative abundance of m/z 180 and the smallest of $[M]^{\bullet+}$. This is attributed to the stability of the delocalized carbazolyl radical produced from **1a** by homolytic cleavage (eq 1, $R^{\bullet} = {}^{\bullet}NC_{12}H_8$), together with relief of strain from unfavorable nonbonded interactions in $[M]^{\bullet+}$ of **1a**.[18] Compound **2a** also exhibits somewhat less $[M]^{\bullet+}$, in accord with the stabilization by resonance of the product carbazolylmethyl radical (eq 1, R = ${}^{\bullet}CH_2NC_{12}H_8$). Such fragmentation from $[M]^{\bullet+}$ of compounds **3a–5a** would produce relatively unstabilized primary alkyl radicals (eq 1, $R = {}^{\bullet}CH_2(CH_2)_{n-2}NC_{12}H_8$), and uniformly higher amounts of $[M]^{\bullet+}$ are observed.

Further loss of $H_2CN^{\bullet}$ from the ion at m/z 180 occurs apparently with contraction of the central ring to give biphenylene radical ion $[C_{12}H_8]^{\bullet+}$ and accounts for the similar abundances at m/z 152 for all but **7a**. Such a stable ion structure would seem to excuse this violation of the even-electron rule. The molecular ion of **7a** also undergoes loss of $H_2CN^{\bullet}$ to give the fragment at m/z 139 with relative abundance 8.0% at 70 eV (not shown in Table I). Previous precise mass measurements have shown that this loss of 28 amu is from expulsion of $H_2CN^{\bullet}$ and not C_2H_4.[30]

Loss of carbazolyl radical from $[M]^{\bullet+}$ gives $[M - 166]^+$, which is most important for **1a**, where it corresponds to m/z 180 as discussed above. Such α-cleavage, however, does not explain carbazolyl loss observed for **4a**. The ion at m/z 222 increases in relative abundance at 20 eV (and is very important in the CI spectrum as discussed below). This suggests that the two aromatic ring systems approach each other, and elimination of the radical proceeds in a concerted process with ring closure to form a quaternary ammonium ion containing a spiro pyrrolidine ring (eq 2).



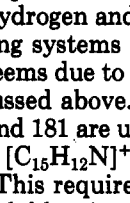
(2)

m/z 222

The complementary carbazolyl ion at m/z 166 is observed at 2% or less for **1a–6a**. It is much stronger for the small molecule **7a**, where it is also $[M - H]^+$ and where, as already mentioned, there are few other favorable fragmentation opportunities. Homolytic cleavage adjacent to the radical-charge site on nitrogen then accounts for its formation from **7a**.

Expulsion of a carbazole *molecule* from $[M]^{\bullet+}$ corresponds to $[M - 167]^{\bullet+}$, observed with similar low abundances at 70 eV for **1a–3a** and **5a**. This must involve a hydrogen migration, and the ion shows increased relative abundance at 20 eV for **3a** and **5a**. To account for its formula, the ion will have a double bond or a ring in the side chain if its aromatic ring system is not disturbed. For **3a**, a 1-propenyl chain would be conjugated to a radical-charge site on nitrogen, and for **5a**, this may be a 1-pentenyl or cyclopentyl group. In both cases, the position α to nitrogen would lose hydrogen and again would require proximity of the two ring systems in $[M]^{\bullet+}$. Failure to observe this ion for **4a** seems due to competing loss of the carbazolyl radical, discussed above.

The ions at m/z 206 and 181 are uniquely abundant for **3a**. The first would be $[C_{15}H_{12}N]^+$, formed from $[M]^{\bullet+}$ with loss of $C_{12}H_{10}N^{\bullet}$. This requires a double hydrogen migration to the carbazolyl leaving group. A cyclization of the ion to give a structure containing an additional six-membered ring, as shown, would explain this observation of $[M - 168]^+$ for **3a** only. This process also suggests interaction of the two ring systems of the molecular ion, which should be sterically most favorable for **3a**.[21] The ion at m/z 181 is formed in a low-energy process and is formulated as $[C_{13}H_{11}N]^{\bullet+}$ with concomitant production of $C_{14}H_{11}N$, apparently *N*-vinylcarbazole. The process is



m/z 206

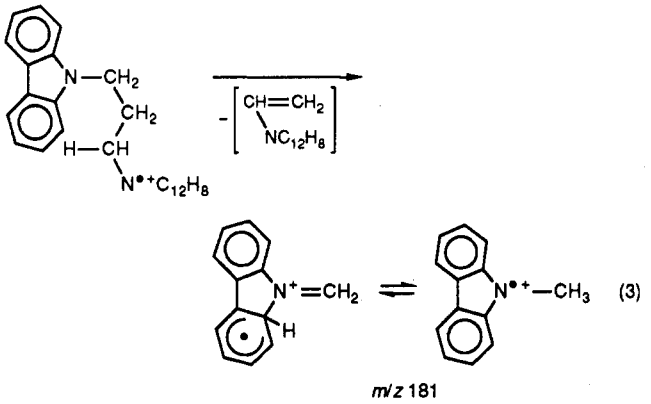
(32) Chupka, W. A. *J. Chem. Phys.* **1971**, *54*, 1936.
(33) Riepe, W.; Zander, M. *Z. Naturforsch.* **1969**, *24a*, 2017.
(34) Alternatively, this ion may have a ring-expanded protonated phenanthridine structure by analogy with $[M - H]^+$ from *N*-methylpyrrole and *N*-methylindole. Marx, M.; Djerassi, C. *J. Am. Chem. Soc.* **1968**, *90*, 678.

Table II. Relative Abundances of (Nitrocarbazolyl)alkane Ions as Percent of Total[a] (EI at 70 eV)

ion	1b	2b	3b	4b	5b	6b	7b
$[M]^{\bullet+}$	1.4[b]	4.3[b]	15.4[b]	13.8[b]	7.8[b]	28.5[b]	37.2[b]
	(391)	(405)	(419)	(433)	(447)	(240)	(212)
$[M]^{2+}$	1.3		3.7	3.6	3.7	0.6	
	(195.5)		(209.5)	(216.5)	(223.5)	(120)	
$[M - NO]^+$			b	b	0.5[b]	2.0	15.3[b]
			(389)	(403)	(417)	(210)	(182)
$[M - NO_2]^+$						3.4	20.4
						(194)	(166)
$[M - NO - CO]^+$						0.6	4.5
						(182)	(154)
m/z 225	2.6	0.7	4.6	3.2	2.8	34,3	
m/z 180	71.5	73.5[b]	55.4	64.0	64.2		
m/z 179	4.7	2.7	6.5	6.1	5.8	21.1	
m/z 166	2.5	0.8	1.6	1.3	1.2	1.6	–[c]
m/z 152	8.2	8.4	6.0	5.6	5.2		

[a] See footnote a, Table I. [b] These abundances increase at 20 eV. [c] See $[M - NO_2]^+$.

explained as a rearrangement with a six-member cyclic transition state giving an iminium ion, which may tautomerize to the *N*-methylcarbazole ion (eq 3). Either



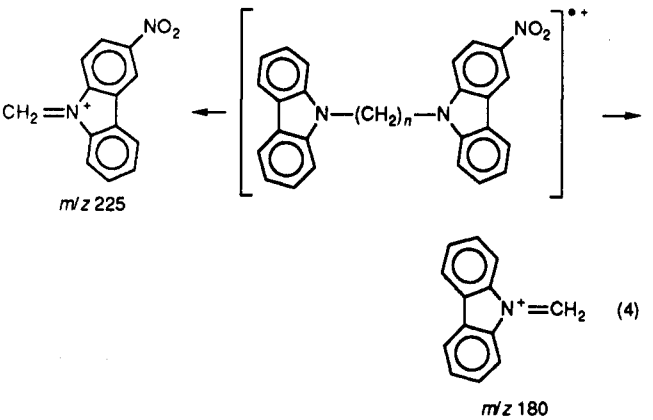
m/z 181 (3)

structure provides spin and charge delocalization. The analogous process yielding $[C_7H_8]^{\bullet+}$ from 1,*n*-diphenylalkanes is reportedly most favored also when $n = 3$.[35]

Electron Ionization of Nitrodicarbazolylalkane Derivatives. The EI spectra of simple nitroarenes have been interpreted.[36] Table II includes the relative abundances at 70 eV for the principal ions from **1b–7b**. Results for **6b** and **7b** agree with a previous report, which includes metastable processes.[31]

As with **7a** and **6a**, **7b** and, secondarily, **6b** show the most abundant $[M]^{\bullet+}$ of the series of nitro derivatives. The molecular ion is less abundant in **7b** than in **7a** because **7b** undergoes fragmentation involving the nitro group, with loss of NO• (in a low-energy rearrangement), $NO_2^{\bullet}$, NO• + CO, and $NO_2^{\bullet}$ + HCN. All such fragments are observed, although to a much smaller extent, with **6b**, but they are negligible for **1b–5b**, where cleavages as for **1a–5a** become much more important. For the larger molecules, with **1b** a possible exception, the nitro group has little influence on the abundance of $[M]^{\bullet+}$ or of $[M]^{2+}$. This would be expected if, in the radical cations, the charge largely resides on the unnitrated carbazole ring, and, in the dications, a single charge residues on each carbazole ring. There is virtually no $[M]^{2+}$ seen for **6b** and **7b** because the electron-withdrawing nitro function should make the nitrocarbazole dication, with two positive charges necessarily on the same carbazole nucleus as the nitro substituent, considerably less favorable than $[M]^{\bullet+}$.

In the nitrodicarbazolylalkanes **1b–5b**, homolytic cleavage α to an amine function can give either m/z 225 or 180, depending on whether charge is retained on the nitrocarbazole iminium chromophore or on the carbazole iminium chromophore, respectively (eq 4). For **6b**, containing a nitrocarbazole ring system alone, m/z 225 dominates the spectrum, but for each of **1b–5b**, m/z 180 is favored over m/z 225 by at least a factor of 10. This clearly reflects the destabilizing effect of the nitro group on a positively charged ring system, so that the positive charge comes to reside preferentially on the unnitrated ring system. Subsequent fragmentation of the ion at m/z 180 accounts for that at m/z 152 as discussed above. The greatest relative abundance of the iminium ion at m/z 180 is shown by **1b**, in accord with the favorable formation of this ion from **1a**.



(4)

Formation of the ion with m/z 180 means that the product ion is devoid of a nitro group, which instead must be retained on the neutral radical. The very low abundance of $[M]^{\bullet+}$ observed for **1b** compared to those of **1a** and **3b–5b** indicates a significant destabilizing effect of the nitro substituent on $[M]^{\bullet+}$ of **1b**. Delocalization of charge between the two carbazole rings of **1a** is enforced by their proximity and is not stabilizing.[18] A similar interaction in **1b** would involve a nitrocarbazole ring and thus account for the destabilization. With the longer polymethylene chains of **3b–5b**, the destabilization of $[M]^{\bullet+}$ by the nitro group is much less important, and the relative abundances of $[M]^{\bullet+}$ and the ion at m/z 180 are close to those observed for **3a–5a**.

Loss of $NO_2^{\bullet}$ from the ion at m/z 225 accounts for the comparable abundances of that at m/z 179, as observed for all nitro derivatives (except, of course, **7b**). This $[C_7H_9N]^{\bullet+}$ is identical or isomeric to that formed by **1a** in a different process discussed above.

The carbazolyl ion at m/z 166 is minor with similar abundances among the nitro derivatives as for the unnitrated dicarbazolylalkanes. The negligible effect of the nitro group on formation of this species supports our supposition that fragmentation is initiated from a radical-charge site on the amine nitrogen of the unnitrated ring system. Accordingly, an analogous nitrocarbazolyl ion at m/z 211 is not observed.

Chemical Ionization. Relative ion abundances for **1a–7a** are listed in Table III and for **1b–7b** in Table IV. One expects methane CI spectra to be dominated by the even-electron protonated molecule $[M + H]^+$. This is observed here to nearly the same extent for all except **1a** and **1b**, which show unusually facile fragmentation producing the ions at m/z 180. In addition, **4a** produces the ion at m/z 222. These fragments were also seen in EI. Methane–plasma adducts $[M + C_2H_5]^+$ and the minor $[M + C_3H_5]^+$ in most cases parallel the relative abundances

(35) Kuck, D. *Mass Spectrom. Rev.* **1990**, *9*, 187.
(36) Meyerson, S.; Puskas, I.; Fields, E. K. *J. Am. Chem. Soc.* **1966**, *88*, 4974 and references therein.

Table III. Relative Abundances of Carbazolylalkane Ions as Percent of Total[a] (CH_4 CI)

ion	1a	2a	3a	4a	5a	6a	7a
$[M + C_3H_5]^+$			0.8		0.5	2.1	1.8
			(415)		(443)	(236)	(208)
$[M + C_2H_5]^+$		8.3	11.1	1.9	6.1	11.2	11.1
		(389)	(403)	(417)	(431)	(224)	(196)
$[M + H]^+$	4.1	53.7	65.4	25.3	56.7	61.5	63.0
	(347)	(361)	(375)	(389)	(403)	(196)	(168)
$M^{\cdot+}$	3.7	16.5	17.9	12.7	18.6	22.2	21.3
	(346)	(360)	(374)	(388)	(402)	(195)	(167)
$[M + C_2H_5 - 167]^+$	12.4						
	(208)						
$[M + H - 167]^+$	–[b]	4.7	1.3	44.6			
	(180)	(194)	(208)	(222)			
m/z 180	79.9	16.9	3.5	15.5	18.1	3.0	

[a] See footnote, *a*, Table I. [b] See m/z 180.

Table IV. Relative Abundances of (Nitrocarbazolyl)alkane Ions as Percent of Total[a] (CH_4 CI)

ion	1b	2b	3b	4b	5b	6b	7b
$[M + C_3H_5]^+$		2.1	3.2	1.5	1.9	3.6	3.3
		(446)	(460)	(474)	(488)	(281)	(253)
$[M + C_2H_5]^+$	0.3	9.5	10.2	12.5	9.5	10.5	12.2
	(420)	(434)	(448)	(462)	(476)	(269)	(241)
$[M + H]^+$	7.8	55.9	74.4	72.5	74.0	72.5	71.1
	(392)	(406)	(420)	(434)	(448)	(241)	(213)
$[M]^{\cdot+}$	0.9	8.2	8.8	10.1	11.3	7.3	5.9
	(391)	(405)	(419)	(433)	(447)	(240)	(212)
$[M + H - OH]^{\cdot+}$						1.7	1.8
						(224)	(196)
$[M + H - NO_2]^{\cdot+}$	4.6					1.5	2.1
	(346)					(195)	(167)
m/z 208	15.7						
m/z 180	70.7	21.1	3.4	3.4	3.4		

[a] See footnote *a*, Table I.

of $[M + H]^+$. Also observed in each case is the molecular radical ion $[M]^{\cdot+}$, with significant and compound-dependent relative abundances. This appears to result mainly from electron transfer from M to the plasma, which is exothermic and, therefore, likely if the ionization energy of M is below 8.4 eV.[37] The ionization energy of **7a** is reported as 7.2 eV,[33] and those of the other dicarbazolylalkanes should be similar. The nitro derivatives should have somewhat higher ionization energies, and this is reflected by their lower abundances of $[M]^{\cdot+}$. The markedly lower abundances of $[M]^{\cdot+}$ for **1a** and **1b** are attributed to their easy fragmentation, as discussed above for EI. Similar considerations affect fragmentation of $[M + H]^+$, as described below.

The iminium fragment $[C_{13}H_{10}N]^+$ at m/z 180 dominates the 70 eV EI spectra of all the present compounds except **6b** (and, of course, **7a** and **7b**). This fragment is found in the CI spectra as well, but with widely varying abundances. The m/z 180 ion is strongest for **1a** (80% RA) and **1b** (70% RA) and weakest for **3a**, **6a**, and **3b–5b** (<4% RA). The ethylated analogue of this fragment, arising from $[M + C_2H_5]^+$, is seen at m/z 208 for **1a** and **1b**. The $[M + H]^+$ ion is correspondingly weak (<8% RA) for both **1a** and **1b**. Fragmentation of $[M]^{\cdot+}$ for **1a** and **1b** to form the relatively stable iminium ion with m/z 180 (but not m/z 225) occurs under low-energy ionization and must be facile. This result bears on product studies of electron-transfer nitration in solution, where **1a** has been found to be the only dicarbazolylalkane to afford nitrocarbazole (a minor product formed as a mixture of 1- and 3-positional isomers, in addition to **1b**). Facile fragmentation to form iminium ion also is observed from $[M + H^+]$ of **1a**, which suggests that the nitrocarbazole formed in solution may result by fragmentation of either the radical cation or the Wheland intermediate, or perhaps both.[38]

Observation of an ion with m/z 208 in the CI spectra of **1a** and **1b** is noteworthy. We might hypothesize attack at an amine nitrogen of 1 by the electrophile E^+, which may be either a proton from $[CH_5]^+$ or ethyl cation. However, for cleavage of an exocyclic N–C bond with charge migration, m/z 208 is not explained, as the ethyl group would accompany the neutral fragment, *N*-ethylcarbazole ($C_{12}H_8N$–E for E = C_2H_5), as shown in eq 5. Furthermore, **1b** would be expected to give m/z 225 following addition of E^+ to the more basic carbazole nitrogen, which is contained within the unnitrated carbazole ring, and no m/z 225 fragment is seen.

$$C_{12}H_8NCH_2NC_{12}H_8 \xrightarrow[?]{E^+} C_{12}H_8N^+(E)CH_2NC_{12}H_8 \longrightarrow C_{12}H_8NE + CH_2{=}N^+C_{12}H_8 \quad (5)$$

m/z 180

Although *N*-alkylanilines are protonated at the nitrogen atom,[39] the nitrogen atom in carbazoles is sp^2 hybridized and much less basic. Alternatively, attack by E^+ at the nitro group, as reported for various nitrobenzenes,[26,40] would be consistent with the presence of m/z 180 and absence of m/z 225 for **1b**. However, this would be so for either E = H or C_2H_5, and E would again accompany the neutral fragment; thus, m/z 208 is still not explained.

Finally, we consider E^+ to attack at a carbon of the unnitrated carbazole ring system.[41] A subsequent α-homolytic cleavage with a hydrogen shift via a cyclic transition state between the ring systems would correctly give m/z 180 for **1a** or **1b** if E = H and m/z 208 if E = C_2H_5. The neutral product would be a carbazole or a nitrocarbazole. That electrophilic attack is preferred at the aromatic ring rather than at the nitrogen atom is evidenced also by secondary ion emission from carbazole in acid solution.[42] The following equation illustrates attack at

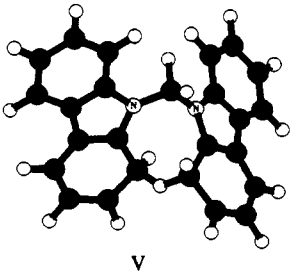
(37) (a) Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983; p 66. (b) We thank a referee for pointing out that $[M]^{\cdot+}$ may form also by residual EI under imperfect CI conditions.

(38) Iminium ion also forms easily from $[M]^{\cdot+}$ and $[M + H]^+$ of **1b**, and formation of nitrocarbazole from secondary photolysis of **1b** has not been excluded.

(39) Pachuta, S. J.; Isern-Flecha, I.; Cooks, R. G. *Org. Mass Spectrom.* **1986**, *21*, 1.

(40) Kruger, T. L.; Flammang, R.; Litton, F.; Cooks, R. G. *Tetrahedron Lett.* **1976**, *4555*.

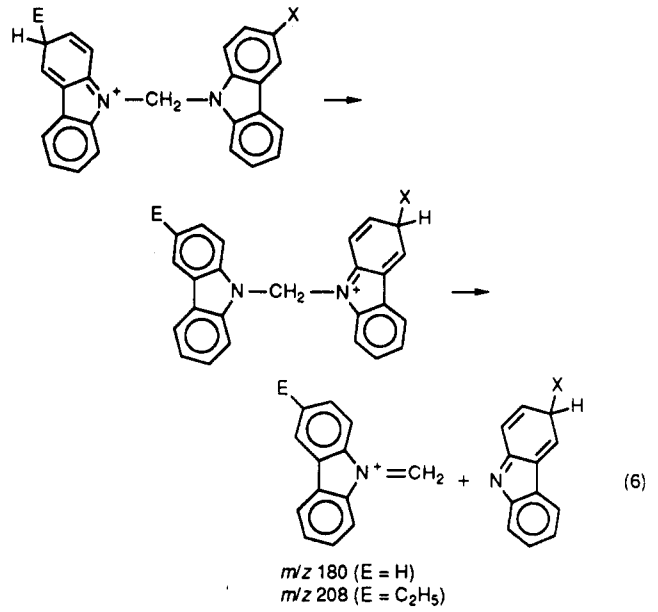
(41) Rapid equilibration (for example, by [1,5] sigmatropic rearrangements) may occur before the interannular migration. Related processes, such as (i) attack on carbazole nitrogen followed by sigmatropic rearrangement to carbon, (ii) attack on the nitro group followed by migration of E^+ to the unnitrated ring, or (iii) attack on the nitrated carbon followed by migration of NO_2^+ to the unnitrated ring, are not excluded, however. Examination of molecular models suggests a transition state involving migration of a substituent between C1 of one carbazole ring and C1′ of the other, as in V, would be the least strained.



V

(42) Liebman, C. P.; Todd, P. J.; Mamantov, G. *Org. Mass Spectrom.* **1988**, *23*, 634.

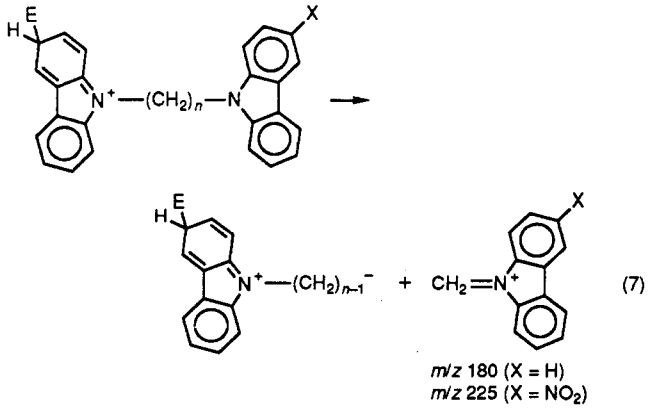
a 3-position, but attack at another position cannot be distinguished from these results as long as an interannular hydrogen shift precedes (or accompanies) cleavage.[41]



(6)

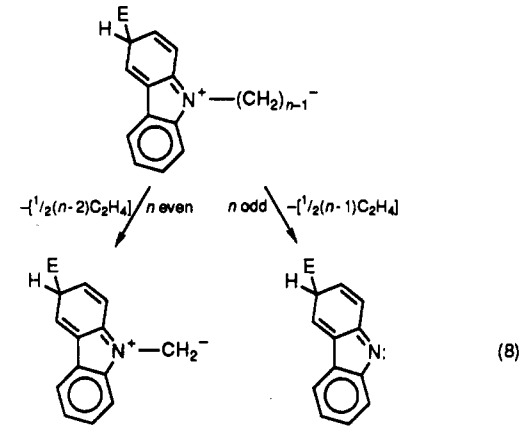
Interestingly, the abundance ratio of m/z 180 to m/z 208 for **1a** or **1b** (6.4 and 4.8, respectively, if the minor contribution of $[M + H - NO_2]^{\bullet+}$ is added to that of m/z 180 for **1b**) is approximately equal to the ratio of $[M + H]^+$ to $[M + C_2H_5]^+$ for **3a**, **6a**, **7a**, and **3b–7b** (mean 6.3 ± 0.9 sd for these eight compounds), where these ions undergo little fragmentation. In other words, the formation of m/z 180 and m/z 208 depends essentially on whether it is H^+ or $C_2H_5^+$ which reacts with **1**, after which facile hydrogen migration and expulsion of neutral carbazole or nitrocarbazole occur regardless.

This mechanism also explains the much lower yields of m/z 180 and 208 for **2–5**, where carbazole cannot be produced directly. For example, m/z 180 is observed to be about 5 times less abundant for CI spectra of **4b** and **5b** than for CI of **4a** and **5a**, and at least 20 times less abundant than for CI of **1a** or **1b**. Ion of m/z 208 is not seen for any **2–5** (except for the special case of **3a**, where m/z 208 also corresponds to $[M + H - \text{carbazole}]^+$). Again, attack of E^+ at a 3-position of the unnitrated carbazole ring system is illustrated (eq 7). Heterolytic cleavage of a C–C



(7)

bond as shown in eq 7 would give the ion at m/z 180 when X = H but not when X = NO_2. Neither would m/z 225 be easily produced when X = NO_2, because the electron-withdrawing effect of the nitro group would tend to prevent positive charge migration to that ring system. Therefore, the $[M + E]^+$ adducts of **3b–5b** are relatively stable and abundant. The neutral fragment in eq 7 is shown with a distonic alkide chain. However, concerted loss of C_2H_4 molecules, if necessary, could give an ylide if n is even or the 1*H*- or 3*H*-carbazole (or ethylcarbazole, when E = C_2H_5) isomer if n is odd (eq 8). In the case of **2** (n = 2), the ylide would be formed directly by eq 7 without loss of C_2H_4. The absence of m/z 208 for any **2–5** (except **3a**) indicates that interannular hydrogen migration is limited to $[M + E]^+$ of 1 and does not occur as readily when a longer spacer separates the carbazole rings.



(8)

In the series **2a–5a**, **3a** is anomalous in its low abundance of the m/z 180 fragment and the corresponding high abundance of $[M + E]^+$, as found for **6a** and **7a**. Here we invoke a molecular stabilization optimal for n = 3, where the two ring systems can most easily associate in a sandwich conformation.[18,21] The low fragmentation is explained if the intramolecular association exists prior to attack by E^+, so $[M + E]^+$ retains this association and has relatively less internal energy. The effect is less apparent with EI, where more energy is available from ionization and entropic considerations are more important. Such sandwich-type ground-state association has recently been reported in another series of bichromophoric molecules in solution.[43]

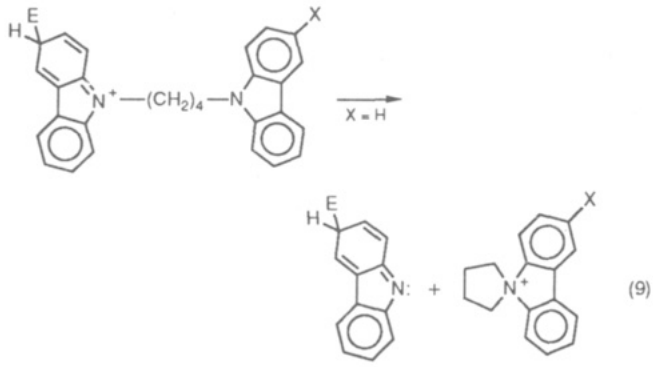
Other than for **1a** and **1b** already discussed, the CI fragment $[M + H - \text{carbazole}]^+$ or $[M + H - \text{nitrocarbazole}]^+$ is abundant only for **4a**, for which this gives the strongest peak in its spectrum, $[C_{16}H_{16}N]^+$ at m/z 222.[44] Investigation of the CI of a series of gaseous 1,n-diaminoalkanes, $H_2N(CH_2)_nNH_2$ with n = 2–8, indicated the n = 4 case similarly showed $[M + H - NH_3]^+$ with the greatest relative abundance. A cyclic pyrrolidinium structure was considered for $[M + H - NH_3]^+$, which could form with anchimeric assistance from protonated diaminobutane.[45] This cyclic structure has the lowest enthalpy of six likely $[C_4H_{10}N]^+$ isomers.[46] The mechanism of formation of $[M + H - \text{carbazole}]^+$ from **4a** likely is analogous. Although the nitrogens of **4a** are less basic than the nitrogen of diaminobutane, which is protonated under CI conditions, electrophilic addition to a ring carbon of **4a** is expected to lead to a similar result (eq 9). A low-energy conformation (IV) for the displacement is accessible. The dramatically lower abundances of $[M + H - \text{carbazole}]^+$ found for **3a** and **5a** demonstrate unambiguously that geometric constraints imposed by the methylene chains

(43) Reynders, P.; Kühnle, W.; Zachariasse, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3929.

(44) Small amounts of $[M + H - 167]^+$ observed for CI of **3a** and, especially, **2a** may arise from analogous cyclizations to form azetidinium and aziridinium rings.

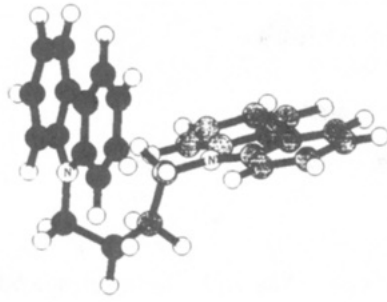
(45) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2699. Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.

(46) Weinkam, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 1032.



(9)

remain important for orientation of the carbazole groups in the gas phase.



IV

The ion $[M + E]^+$ from **4a** eliminates carbazole for E = H, giving m/z 222 (eq 9). This m/z 222 ion should be the same as that produced under EI conditions (eq 2) and indicates that the nitrogen of carbazole is capable of behaving as an effective nucleophile. Consistent with this explanation, $[M + E]^+$ for E = C_2H_5 would eliminate ethylcarbazole by the process shown in eq 9, and again m/z 222 but not $[M + C_2H_5 - \text{carbazole}]^+$ at m/z 250 would be formed. Apparently, the analogous fragmentations do not occur in **4b** because the electron-withdrawing nitro group decreases both the basicity of the carbazolyl function as well as the nucleophilicity of the carbazolyl nitrogen, hindering formation of a bridged $[M + H]^+$ and retarding the displacement.[47]

Of the nitro derivatives, only the lighter **1b**, **6b**, and **7b** show significant, but small, abundances of $[M + H - NO_2]^{\bullet+}$, and only **6b** and **7b** show $[M + H - OH]^{\bullet+}$ in the only violations of the even-electron rule seen here in CI. These processes have been observed in a variety of nitrobenzenes and were attributed to initial protonation at the nitro group.[26,48] Although the protonated nitrobenzenes were found to undergo loss of OH$^\bullet$ more readily than of $NO_2^\bullet$, here loss of $NO_2^\bullet$ is at least as important, especially for **7b**. This is attributed to protonation preferentially at a site other than the nitro group, as well as the more advantageous delocalization of spin and charge in the carbazole ions produced by $NO_2^\bullet$ loss.

Summary and Conclusions

Comparison of dicarbazolylalkanes **1–5** with monocarbazole counterparts **6** and **7** indicates that the dicarbazole materials show a greater tendency to fragment to daughter ions. Iminium ion (m/z 180) is important in all cases for the 70 eV EI spectra of the dicarbazoles. Fragmentations of $[M]^{\bullet+}$ of **1a** and **1b** are exceptionally facile due to formation of the relatively stable iminium ion together with the resonance stabilized carbazolyl (or nitrocarbazolyl) radical. Fragmentation from $[M]^{\bullet+}$ of **2** appears to be facilitated somewhat due to formation of iminium ion and the carbazolylmethyl or (3-nitrocarbazolyl)methyl radical, compared with fragmentation of **3–5**, which produce iminium ion and unstabilized primary radicals.

Fragments similar to those produced by EI are observed, although with different relative abundances, following CI of the dicarbazolylalkanes. Fragmentation of $[M + H]^+$ from **1a** and **1b** also is facile due to formation of iminium ion (m/z 180) together with carbazole or nitrocarbazole. The ions $[M + H]^+$ and $[M + C_2H_5]^+$ are produced with similar respective abundances for **2a**, **3a**, and **5a**. The observation of ethylated iminium ion (m/z 208) for **1a** and **1b** indicates that interannular proton migrations precede or accompany cleavage; products of analogous rearrangements were not observed for carbazoles separated by longer chains. Relatively higher amounts of $[M]^{\bullet+}$ and $[M + H]^+$, and lower amounts of the m/z 180 fragment, for **3a** (but not **3b**) in EI and CI spectra suggest, compared to the respective neutral molecules, that there exists an enhanced stabilization for $[M]^{\bullet+}$ and $[M + H]^+$ of **3a** which is modest, at best.

The carbazole nitrogen of dicarbazolylbutane **4a** (but not **4b**) can function as an internal nucleophile which displaces carbazole from $[M + H]^+$ as well as from $[M]^{\bullet+}$ to form a cyclic pyrrolidinium ion (m/z 222). Chemical ionization for the dicarbazolylalkanes probably proceeds predominantly by addition of ionizing electrophile to a ring carbon, however.

Nitrodicarbazoles prefer positive charge to reside in the unnitrated ring. Ions $[M]^{\bullet+}$ and $[M + H]^+$ for **1b–5b** fragment primarily to unnitrated iminium ions (m/z 180) rather than to nitrated iminium ions (m/z 225). This behavior signifies deactivation of the nitrated carbazole ring toward acceptance of positive charge. Consistent is the inability of the carbazole nitrogen of *either* ring in the $[M]^{\bullet+}$ and $[M + H]^+$ ions of **4b** to serve as an effective internal nucleophile.

Relative abundances of $[M]^{2+}$ from EI of **1a**, **6a** and **3–5** are approximately constant, whereas, for nitrocarbazoles **6b** and **7b**, they are sharply reduced. The abundances of $[M]^{2+}$ for **1b** and **2b** also are relatively low. In contrast, the abundances of $[M]^{\bullet+}$ for **6a** and **6b** are similar (28%) and significantly higher than those for **1a** and **1b** (7% and 1%, respectively). These results are consistent with a diradical structure of $[M]^{2+}$ in which each carbazole substituent of the dicarbazolylalkanes bears a single positive charge. Some interaction between the positively charged rings will occur because of their proximity in $[M]^{2+}$ of **1** and possibly **2**, decreasing their stability.

The finding that compound **3a** is somewhat less reactive than the other dicarbazolylalkanes studied, whereas **1a** and **1b** are exceptionally reactive under EI as well as CI conditions, is in accord with the chemistry observed for the radical cations in solution.[18] Interestingly, the enhanced propensity for fragmentation of $[M]^{\bullet+}$ (and/or $[M + H]^+$) from **1b** also may be found in the solution phase electron-transfer reactions of this compound, where indication of cleavage of the N–CH_2 bond is observed.[49] Thus the gas phase ions of the dicarbazolylalkanes examined in this study exhibit selectivities comparable to their solution-phase counterparts. This may be expected for CI and low-energy EI spectra, but is observed even for 70-eV EI spectra. The evidence suggests efficient internal relaxation

(47) The nitro group also provides an alternative site for attack by E^+, obviating this fragmentation process.

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mechanisms operative in these moderately complex bichromophoric molecules.

Acknowledgment. J.M. gratefully acknowledges support from the Research Challenge Program administered by the Ohio Board of Regents and thanks Professor R. J. Baker for molecular mechanics and drawing algorithms.

Registry No. **1a**, 6510-63-0; **1a**·$C(NO_2)_4$, 124854-89-3; **1b**, 136954-47-7; **2a**, 25557-82-8; **2a**·$C(NO_2)_4$, 124822-76-0; **2b**, 136954-48-8; **3a**, 25837-66-5; **3a**·$C(NO_2)_4$, 124822-77-1; **3b**, 136954-49-9; **4a**, 22335-46-2; **4a**·$C(NO_2)_4$, 124822-78-2; **4b**, 136954-50-2; **5a**, 60834-40-4; **5a**·$C(NO_2)_4$, 124822-79-3; **5b**, 136954-51-3; **6a**, 86-28-2; **6a**·$C(NO_2)_4$, 124822-80-6; **6b**, 86-20-4; **7a**, 86-74-8; **7a**·$C(NO_2)_4$, 136954-52-4; **7b**, 3077-85-8; 4-$MeC_6H_4SO_2O(CH_2)_2OSO_2C_6H_4Me$-4, 6315-52-2; carbazole, 86-74-8.

Supplementary Material Available: NMR data and spectra for compounds **1a–6a** and spectra for **1b–6b** (24 pages). Ordering information is given on any current masthead page.

Origin of "Hetero Effect" on Nitrogen Inversion. Comparison of Hydroxylamines and Aminoxide Anions

Charles L. Perrin,* John D. Thoburn, and Seth Elsheimer

Department of Chemistry 0506, University of California, San Diego, La Jolla, California 92093-0506

Received July 15, 1991

Rate constants for nitrogen inversion in *N*-benzyl-*N*-methylhydroxylamine, *N*,*N*-diethylhydroxylamine, 1-hydroxy-2,2,4,4-tetramethylpyrrolidine, their conjugate bases, and their *O*-acetyl derivatives in dimethylformamide-d_7 were determined based on the ^1H NMR coalescence temperatures. Relative to –OH, the $-O^-$ substituent ought to either raise the barrier to inversion owing to stronger lone-pair repulsions or lower the barrier owing to weaker σ-inductive effects. Yet nearly identical barriers to inversion, $\Delta G^\ddagger$ = 12.0–13.3 kcal/mol, are observed for both the hydroxylamine and its conjugate base. Since the observed barrier is little changed upon deprotonation, it is concluded that the π-repulsive and σ-inductive contributions must be nearly equal.

Introduction

Substituent Effects in Nitrogen Inversion. A nitrogen atom with three substituents and a nonbonding lone pair of electrons has a pyramidal geometry capable of inverting its configuration. The ground state has a nominally sp^3-hybridized nitrogen atom with the lone pair occupying an orbital that is approximately sp^3. The transition state has an sp^2-hybridized nitrogen with the lone pair in a pure p orbital.

The rate at which the nitrogen inverts is subject to steric, conjugative, inductive, and angle-constraint effects of substituents.[1-4] Electronegative heteroatoms such as oxygen, nitrogen, or halogen increase the barriers to nitrogen inversion. Thus, the barriers increase across the first row from R_2N–CH_3 (7.4 kcal/mol) to R_2N–NH_2 (8.5 kcal/mol) to R_2N–OH (13.1 kcal/mol) to R_2N–F (20 kcal/mol). Extreme cases are *N*-chlorooxaziridine and dioxaziridine (which also include a contribution from a three-membered ring) as well as NF_3, for which calculated barriers are 44.2,[5] 55.6,[6] and 78.2 kcal/mol,[7] respectively.

These substituents have both a σ-inductive electron-withdrawing character and a π-repulsive character due to the lone pairs. According to simple rules for hybridization,[8] atomic p character concentrates in orbitals directed toward electronegative substituents. This results in more s character in the nitrogen lone pair, which in the transition state must occupy a pure p orbital. The σ-inductive effect of electronegative substituents therefore increases the barrier to inversion. (An equivalent approach to this effect is in terms of HOMO–LUMO mixing.[9]) There is also a π-repulsive effect, associated with overlap of the lone pair with π orbitals on adjacent atoms. Lone-pair repulsions create a destabilization which is greatest in the transition state, since overlap with a pure p orbital is maximum. This too increases the barrier to inversion.

Both of these effects must be operative. In the absence of lone pairs, barriers to phosphorus inversion in RP(Ph)M$(CH_3)_3$ increase with the electronegativity of M.[10] The conjugative effect of electron-withdrawing acyl groups to reduce the barrier to nitrogen inversion in aziridines is well-known.[11]

The relative contribution of these two effects of adjacent heteroatoms is a long-standing question, which most researchers have explicitly despaired of answering.[1-4,9,12] Does the increased barrier arise primarily because of the inductive effect of electronegative substituents or because of the repulsion of their lone pairs? The latter seems more likely, since repulsions in the π system are generally stronger than σ-inductive effects. It has not been possible to distinguish these, because they usually operate in the same direction. Molecular-orbital calculations[13] can re-

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