

chromatography using petroleum ether/ethyl acetate eluant (9:1,  $R_f = 0.7$ ). Crystallization from ethanol gave orange crystals of 3,4-diethyl-3-(4-nitrophenyl)-4-[4-(dimethylamino)phenyl]hexane (**1d**) in 60% yield, mp 105–106 °C. The crystals for the X-ray analysis were grown from acetonitrile.

**1d**:  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ ) 7.97 (d,  $J = 9.0$  Hz, 2 H), 7.04 (d,  $J = 9.0$  Hz, 2 H), 6.71 (d,  $J = 8.5$  Hz, 2 H), 6.52 (d,  $J = 8.5$  Hz, 2 H), 2.92 (s, 6 H), 2.10 (m, 2 H), 1.96 (m, 6 H), 0.73 (t,  $J = 8.2$  Hz, 12 H);  $^{13}\text{C NMR}$  (125.8 MHz,  $\text{CDCl}_3$ ) 153.6, 148.2, 145.2, 131.0, 130.6, 130.4, 121.1, 110.6, 52.9, 51.2, 40.4, 25.5, 25.4, 10.5, 10.4; MS-EI ( $m/e$ , relative intensity) 353 ( $\text{P}^+ - \text{Et}$ , 0.5), 335 (2), 324 (2), 306 (14), 190 (100), 175 (6), 162 (17), 160 (41), 148 (8), 145 (13), 144 (11), 136 (10), 134 (13), 130 (10), 116 (16), 91 (9), 77 (6); MS-CI ( $\text{CH}_4$ ,  $m/e$ , relative intensity) 228 (3), 218 (2), 190 (100), 174 (4), 162 (20).

5,6-Dibutyl-5-(4'-nitrophenyl)-6-phenyldecane (**2b**) was prepared by nitration of **2a** in acetic anhydride as described for **1b** above. The column-purified product crystallized from ethanol to fine colorless crystals: mp 85–86 °C;  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ ) 7.96 (d,  $J = 9.0$  Hz, 2 H), 7.13 (m, 3 H), 7.01 (d,  $J = 9.0$  Hz, 2 H), 6.86 (m, 2 H), 1.97 (m, 2 H), 1.88 (m, 6 H), 1.26 (m, 8 H), 1.08 (m, 2 H), 0.98 (m, 6 H), 0.84 (m, 12 H); IR 3045, 2935, 2855, 1590, 1500, 1445, 1360, 1330, 1085, 830, 740, 710, 680; MS-EI ( $m/e$ , relative intensity) 365 (9), 347 (7), 249 (10), 203 (20), 163 (12), 147 (25), 133 (20), 118 (41), 105 (19), 91 (100), 57 (11).

Preparation of 5,6-dibutyl-5-(4-nitrophenyl)-6-(3-fluorophenyl)decane (**2c**) was analogous to that described for **2b**. An equimolar mixture of 5-phenylnonan-5-ol and 5-(3-fluorophenyl)nonan-5-ol (each prepared from 5-nonanone and the corresponding phenylmagnesium bromide) were coupled using the procedure described for **1a**.<sup>13</sup> The crude mixture, including the 5,6-dibutyl-5-phenyl-6-(3-fluorophenyl)decane cross-coupling product, was nitrated in acetic anhydride as described above. Flash column chromatography using  $\text{CH}_2\text{Cl}_2$ -hexane (1:9), followed by HPLC separation with 100% hexane, afforded pure **2c**. Crystallization from ethanol at room temperature gave colorless crystals: mp 104.5–105.5 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 7.98 (d,  $J = 9.0$  Hz, 2 H), 7.04 (d,  $J = 9.0$  Hz, 2 H), 7.00–7.15 (m, 1

H), 6.85 (m, 1 H), 6.60 (m, 2 H), 1.75–2.04 (m, 8 H), 1.27 (m, 8 H), 0.85–1.12 (m, 8 H), 0.85 (m, 12 H); IR 3065, 2925, 1930, 1800, 1585, 1505, 1450, 1365, 1330, 1250, 1220, 1205, 1150, 1090, 995, 935, 870, 835, 760, 715, 685; MS-EI ( $m/e$ , relative intensity) 423 (3), 383 (9), 365 (24), 325 (8), 309 (7), 249 (15), 221 (13), 215 (8), 165 (17), 163 (35), 151 (16), 146 (13), 136 (36), 133 (12), 129 (14), 123 (27), 115 (17), 109 (100), 91 (16), 69 (10).

2,3,4,5-Tetramethyl-3,4-diphenylhexane (**3a**) obtained as ca. 1:1 mixture of *meso* and *dl* isomers was nitrated by the procedure indicated for **1b**. The resulting yellow oil was submitted multiple times to flash column chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  gradient, or hexane/ethyl acetate gradient), but could not be separated cleanly. Repeated preparative HPLC (70% hexane–30%  $\text{CH}_2\text{Cl}_2$ ) was finally successful in affording pure *erythro* and *threo* isomers, of which only the *threo* crystallized (colorless crystals from ethanol, mp 115–117 °C). *erythro*-**3b**:  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ ) 7.89 (d,  $J = 9.0$  Hz, 2 H), 7.12 (m, 4 H), 6.80–7.00 (br, 3 H), 2.87 (sep,  $J = 6.5$  Hz, 2 H), 1.42 (s, 3 H), 1.27 (s, 3 H), 1.22 (d,  $J = 6.5$  Hz, 3 H), 1.19 (d,  $J = 6.5$  Hz, 3 H), 0.47 (d,  $J = 6.5$  Hz, 3 H), 0.41 (d,  $J = 6.5$  Hz, 3 H); MS-EI ( $m/e$ , relative intensity) 226 (5), 193 (29), 147 (100), 131 (14), 117 (12), 115 (13), 105 (70), 103 (10), 91 (77), 77 (11). *threo*-**3b**:  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ ) 8.13 (d,  $J = 9.0$  Hz, 2 H), 7.60 (d,  $J = 9.0$  Hz, 2 H), 7.21–7.40 (m, 5 H), 1.70 (m, 1 H), 1.62 (m, 1 H), 1.53 (s, 3 H), 1.50 (s, 3 H), 1.10 (d,  $J = 6.0$  Hz, 3 H), 1.05 (d,  $J = 6.0$  Hz, 3 H), 0.36 (d,  $J = 6.0$  Hz, 3 H), 0.28 (d,  $J = 6.0$  Hz, 3 H); MS-EI ( $m/e$ , relative intensity) 312 (6), 249 (6), 226 (4), 193 (20), 150 (16), 147 (83), 131 (40), 117 (24), 115 (20), 105 (92), 103 (20), 91 (100), 84 (15), 77 (20), 69 (21).

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**Supplementary Material Available:** Final atomic coordinates, bond lengths, bond angles, torsional angles, and anisotropic thermal parameters for **1b**, **1c**, **1d**, **2b**, **2c**, and **3b** as well as NMR spectra of these compounds (60 pages); listing of observed and calculated structure factors (91 pages). Ordering information is given on any current masthead page.

## Gas-Phase Chemistry of the Negative Ions Derived from Azo- and Hydrazobenzene

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The proton affinities of the azobenzene radical anion and the conjugate base of hydrazobenzene have been determined to be 1465  $\text{kJ mol}^{-1}$  and 1514  $\text{kJ mol}^{-1}$ , respectively, with the use of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source. The proton affinities lead in combination with a measured electron affinity of azobenzene (55  $\text{kJ mol}^{-1}$ ) to a N–H bond dissociation energy (BDE) of 306  $\text{kJ mol}^{-1}$  for hydrazobenzene while the N–H BDE of the  $\text{PhNH}\dot{\text{N}}\text{Ph}$  radical is estimated to be 208  $\text{kJ mol}^{-1}$ . The difference between the N–H BDE values of 98  $\text{kJ mol}^{-1}$  approximates the  $\pi$ -bond energy of the nitrogen–nitrogen bond in azobenzene. The reaction of the  $\text{Ph}\dot{\text{N}}\text{NPh}$  and  $\text{PhNH}\dot{\text{N}}\text{Ph}$  ions with derivatives of trifluoroacetic acid are characterized. The occurrence of dissociative electron transfer instead of  $\text{S}_{\text{N}}2$  substitution in reactions of the azobenzene radical anion with halogen-substituted methanes is discussed.

### Introduction

The formation and reactivity of organic radical anions in the condensed phase is studied intensely,<sup>1–5</sup> whereas less is known about the gas-phase ion/molecule chemistry of these species. The reports are focused mainly on the determination of positive or negative electron affinities (EA)

and rate constants for exothermic electron-transfer reactions.<sup>6–14</sup> Positive electron affinities are reported for

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several classes of compounds,<sup>6</sup> which form relatively stable radical anions in solution, but so far the interplay between the possible bimolecular reactions of radical anions in the gas phase—electron transfer, proton transfer, hydrogen atom abstraction, or nucleophilic displacement—has been studied almost entirely for carbene<sup>15–22</sup> and nitrene ions.<sup>23–26</sup> Comparison with the condensed phase can be complicated for these ions since they are not as readily formed in solution as in the gas phase and, once formed, rapid reaction with solvent molecules by hydrogen atom abstraction or protonation may occur.<sup>27,28</sup>

The present work was initiated by a desire to investigate the gas-phase ion/molecule chemistry of radical anions that are readily formed in the condensed phase. The radical anion of azobenzene was selected in part because a study of the electrochemical reduction of this compound indicated that the radical anion is less basic than the conjugate base of hydrazobenzene in *N,N*-dimethylformamide (DMF).<sup>29</sup> Determination of the basicity of the radical anion was precluded, however, owing to the rapid reduction of the protonated ion, PhNNHPh, to PhNNHPh under the experimental conditions employed.<sup>29</sup>

The ability of the radical anion of azobenzene and the conjugate base of hydrazobenzene to accept a proton in the condensed phase will be strongly dependent upon their interactions with solvent molecules and counterions. To examine whether the lower basicity of PhNNPh than PhNNHPh in DMF is a result of a molecular property, we have determined the proton affinities (PA(A<sup>-</sup>) equal to the gas-phase acidity,  $\Delta H_{\text{acid}}^{\circ}$ , of HA) of the ions in the gas phase.

**Table I. Occurrence/Nonoccurrence of Proton Transfer in the Reactions of the PhNNPh and PhNNHPh Ions with a Series of Reference Acids**

ion	acid (HA)	$\Delta H_{\text{acid}}^{\circ}$ (HA), <sup>a</sup> kJ mol <sup>-1</sup>	proton transfer <sup>b</sup>
PhNNPh	CH <sub>3</sub> NO <sub>2</sub>	1495	no
	C <sub>2</sub> H <sub>5</sub> SH	1482	no
	H <sub>2</sub> S	1471	no
	CH <sub>3</sub> COOH	1458	yes
	HCOOH	1445	yes
PhNNHPh	PhNH <sub>2</sub>	1533	no
	CH <sub>3</sub> CHO	1533	no
	CF <sub>3</sub> CH <sub>2</sub> OH	1514	minor
	CH <sub>3</sub> NO <sub>2</sub>	1495	yes
	C <sub>2</sub> H <sub>5</sub> SH (CH <sub>3</sub> ) <sub>3</sub> CSH	1487 1475	yes yes

<sup>a</sup> Values from ref 42. <sup>b</sup> See text, reaction time from 3 to 10 s, temperature assumed to be 298 K (see Experimental Section).

The radical anion of azobenzene is reported to be formed in the gas-phase reaction of the superoxide ion, O<sub>2</sub><sup>-</sup>, with hydrazobenzene,<sup>30</sup> and in the reaction of the phenylnitrene radical anion with phenyl azide,<sup>24</sup> but its gas-phase chemistry has not been studied previously. In this work the radical anion is formed by electron attachment to azobenzene in an external chemical ionization source of a Fourier transform ion cyclotron resonance (FT-ICR)<sup>31–37</sup> mass spectrometer.<sup>38</sup> The ions are subsequently extracted from the ion source, accelerated, and passed through a series of ion lenses before they are decelerated and trapped in the ICR cell, where the gas-phase reactions of the ions with added neutrals can be studied at a low pressure (about 10<sup>-7</sup> mbar).

## Experimental Section

The experiments were performed with a Bruker CMS 47X FT-ICR instrument equipped with a 4.7-T superconducting magnet and an external chemical ionization source.<sup>38</sup> The general operation procedure of the instrument has been described in recent papers.<sup>39,40</sup>

Azo- and hydrazobenzene were introduced into the external ion source (temperature 370–420 K) with a heated direct insertion probe (temperature 330–370 K) and CO<sub>2</sub> was added to the ion source until the pressure was about 0.1 mbar.<sup>40</sup> Impact of 70 eV electrons on CO<sub>2</sub> produces positive ions and secondary electrons. The secondary electrons are brought to low kinetic energies by collision with the CO<sub>2</sub> molecules, thus allowing electron capture by azobenzene to occur.<sup>41</sup> This results in excited radical anions, which may be stabilized by collisions with the molecules present in the ion source before the occurrence of electron detachment.

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The conjugate base of hydrazobenzene was generated in the chemical ionization source by proton abstraction with  $(\text{CH}_3)_2\text{C}-\text{HCH}_2\text{CH}_2\text{O}^-$  (formed by dissociative electron attachment to the appropriate nitrite) as the base.

The stable negative ions formed as a result of electron impact on the gas mixture were extracted from the ion source, focused into a beam by a series of ion lenses, and accelerated to a kinetic energy of 3 kV. Subsequently, the ions were transferred into the magnetic field and decelerated to such low kinetic energies that trapping in the cylindrical ICR cell occurred. The voltage on the trapping plates of the cell was normally between -1.0 and -1.5 V.

The ICR cell was filled with ions for a certain time interval (20–40 ms), after which the ion beam was deflected before reaching the deceleration region. Standard ejection procedures were applied in order to study selectively the reactions between the ion of interest and a substrate added to the ICR cell (temperature about 300 K) until the pressure was about  $2 \times 10^{-7}$  mbar.<sup>39</sup> The ions were detected after a variable time delay as described previously.<sup>39</sup> Pulsed-valve addition of Ar to the ICR cell was performed for selected reactions. The valve was open for up to 100 ms, which raised the pressure in the ICR cell up to about  $10^{-3}$  mbar. The pressure in the cell reached the level before addition of Ar within 500 ms after the valve was closed.

**Materials.** The compounds were either commercially available or prepared by standard methods. Hydrazobenzene was recrystallized prior to use.

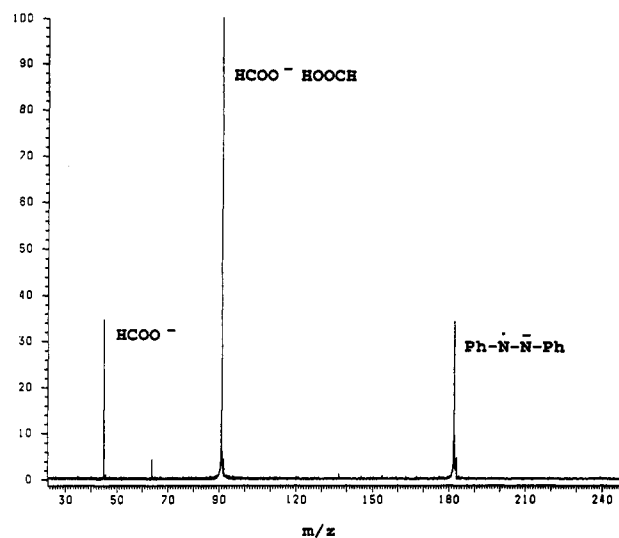
## Results

**Acidity Measurements.** The gas-phase acidity of  $\text{Ph}\ddot{\text{N}}\text{NPh}$  and  $\text{Ph}\text{NHNPh}$  was bracketed by observing the occurrence/nonoccurrence of proton transfer in the reactions of the conjugate bases with a series of reference acids of known acidity. The results are summarized in Table I.

The bracketing method rests upon the assumption that an exothermic proton transfer will be observed while an endothermic reaction will not.<sup>43</sup> In order to test for the occurrence of endothermic reactions, the pressure in the ICR cell was raised up to about  $10^{-3}$  mbar by pulsed-valve addition of Ar (see Experimental Section). During the pressure increase, the ions undergo nonreactive collisions with the Ar atoms, thus allowing for possible excess translational and/or internal energy<sup>44</sup> to be removed before they react with the substrate. Pulsed-valve addition of Ar had no significant effect on the relative abundances of the product ions formed in the reaction of the  $\text{Ph}\ddot{\text{N}}\text{NPh}$  ion with  $\text{CH}_3\text{COOH}$  or in the reaction of the  $\text{Ph}\text{NHNPh}$  ion with  $\text{CF}_3\text{CH}_2\text{OH}$  and with  $\text{CH}_3\text{NO}_2$  (vide infra). These observations imply that the proton-transfer reactions are relatively insensitive to the energy of the ions and/or the ions were at near thermal energy before the pressure increase. From the results in Table I, the gas-phase acidity of  $\text{Ph}\ddot{\text{N}}\text{NPh}$  is placed, therefore, between the values for  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{COOH}$ , that is  $1465 \pm 7$  kJ mol<sup>-1</sup>, whereas the acidity of  $\text{Ph}\text{NHNPh}$  is bracketed between the values for  $\text{PhNH}_2$  and  $\text{CH}_3\text{NO}_2$ , that is  $1514 \pm 19$  kJ mol<sup>-1</sup>. The minor amount of proton transfer from  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\Delta H_{\text{acid}}^\circ = 1514 \pm 15$  kJ mol<sup>-1</sup>)<sup>42</sup> to the  $\text{Ph}\text{NHNPh}$  ion indicates that hydrazobenzene is close in acidity to this compound and that the error limit on the determined value is

(43) The occurrence/nonoccurrence of a thermochemically controlled reaction will be dependent, of course, on the free energy change for the process. For proton-transfer equilibria ( $\text{A}^- + \text{BH} \leftrightarrow \text{AH} + \text{B}^-$ ) in the gas phase, it can be assumed that  $\Delta G^\circ \approx \Delta H^\circ$  since the entropy change in most cases is negligible; see ref 43a,b for discussions of entropy changes of proton-transfer reactions in the gas phase. (a) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 2, Chapter 11, pp 87–122. (b) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* 1979, 56, 1–9.

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**Figure 1.** Spectrum showing the peaks due to the ions present in the ICR cell after the azobenzene radical anion has reacted with  $\text{HCOOH}$  (pressure about  $10^{-7}$  mbar) for 10 s.

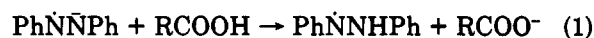
**Table II. Occurrence/Nonoccurrence of Electron Transfer in the Reactions of the  $\text{Ph}\ddot{\text{N}}\text{NPh}$  Ion with a Series of Electron Acceptors**

electron acceptor	$-\Delta G^\circ$ , <sup>a</sup> kJ mol <sup>-1</sup>	EA, <sup>b</sup> kJ mol <sup>-1</sup>	electron transfer <sup>c</sup>
$\text{O}_2$		44 <sup>d</sup>	no
$\text{CH}_3\text{NO}_2$	51	46	no
$\text{CS}_2$	53	49	no
$\text{C}_6\text{F}_6$	62	50	yes
$3\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$		65	yes
$\text{CH}_3\text{COCOCH}_3$	71	67	yes

<sup>a</sup> For electron attachment, values from ref 6. <sup>b</sup> From ref 6. <sup>c</sup> See text, reaction time 3 to 10 s, temperature assumed to be 298 K (see Experimental Section). <sup>d</sup> Reference 51.

somewhat lower than 19 kJ mol<sup>-1</sup>.

Proton transfer from  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$  to the radical anion of azobenzene is followed by formation of a proton-bound dimer of the  $\text{RCOO}^-$  ions (Figure 1 and eqs 1 and 2). A proton-bound dimer,  $\text{CF}_3\text{CH}_2\text{O}-\text{HOCH}_2\text{CF}_3$ ,



is likewise formed as a result of proton transfer from  $\text{CF}_3\text{CH}_2\text{OH}$  to the  $\text{Ph}\text{NHNPh}$  ion. In the case of  $\text{CH}_3\text{NO}_2$ , proton transfer to the  $\text{Ph}\text{NHNPh}$  ion is competing with formation of adduct ions [ $\text{Ph}\text{NHNPh} + \text{CH}_3\text{NO}_2$ ] and with  $\text{C}_2\text{H}_5\text{SH}$  and  $(\text{CH}_3)_3\text{CSH}$  only traces of adducts are observed.

The formation of stable adduct ions under the low pressure conditions commonly employed in FT-ICR ( $\leq 10^{-6}$  mbar) is exceptional since the excess internal energy of the adducts cannot be removed by third-body collisions. Adduct ions have been reported, however, in some instances and radiative stabilization was invoked as the mechanism by which the internal energy is lowered below the threshold for dissociation.<sup>45–50</sup> For the present cases, it can be noted

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**Table III. Product Ions Formed in the Reactions of the PhNNPh and PhNNHPh Ions with Selected Substrates**

substrate	product ion	<i>m/z</i>	rel abundance <sup>a</sup>	
			PhNNPh	PhNNHPh
CF <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	113	no reactions	5
	CF <sub>3</sub> CONPh	188		25
	CF <sub>3</sub> CON(Ph)-NPh	279		70
CF <sub>3</sub> COSC <sub>2</sub> H <sub>5</sub>	CF <sub>3</sub> COS <sup>-</sup>	129	100	20
	CF <sub>3</sub> CONPh	188		15
	CF <sub>3</sub> CON(Ph)-NPh	279		65
(CF <sub>3</sub> CO) <sub>2</sub>	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	113	100	95
	CF <sub>3</sub> CON(Ph)-NPh	279		5
CHBr <sub>3</sub>	Br <sup>-</sup>	79/81	100	50
	<sup>-</sup> CBBr <sub>3</sub>	250-256		50
C <sub>6</sub> F <sub>6</sub>	C <sub>6</sub> F <sub>6</sub> <sup>-</sup>	167	<i>b</i>	30
	(M - 2HF - PhNH)	237		10 <sup>c</sup>
	(M - HF - PhNH)	257		20 <sup>c</sup>
	(M - 2HF)	329		10 <sup>c</sup>
	(M - HF)	349		30 <sup>c</sup>

<sup>a</sup> Approximate values at a reaction time of 3 s and a substrate pressure of 10<sup>-7</sup> mbar in the ICR cell. <sup>b</sup> Only electron transfer to C<sub>6</sub>F<sub>6</sub> is observed, see Table II and text. <sup>c</sup> M = (PhNNHPh + C<sub>6</sub>F<sub>6</sub>).

that no highly exothermic channel is open for the adduct ions. This may increase the lifetime of the encounter complex with the consequence that the probability for photon emission is enhanced.

**EA of Azobenzene.** The results from the bracketing experiments of the EA of azobenzene are collected in Table II. Pulsed-valve addition of Ar to the ICR cell had no noticeable effect on the relative abundances of the radical anions of C<sub>6</sub>F<sub>6</sub> and 3-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN formed as a result of electron transfer from the PhNNPh ion. On the basis of the results in Table II, Δ*G*<sup>o</sup> for reaction 3 can be placed between the values for CS<sub>2</sub> and C<sub>6</sub>F<sub>6</sub>.<sup>43</sup> Reaction 3 is likely



to be associated with a small positive change in entropy since the vibrational frequency of the nitrogen-nitrogen bond and also the barrier toward rotation around that bond may be lower in the radical anion than in the neutral molecule. The expected change in vibrational and rotational entropy adds to the increase in entropy caused by the change from the singlet state of the molecule to the assumed doublet state of the azobenzene radical anion (Δ*S*<sub>elec</sub><sup>o</sup> = *R* ln 2) ≈ 6 J mol<sup>-1</sup> K<sup>-1</sup>.<sup>52</sup> Due to lack of the necessary data, it is not possible to calculate the change in entropy caused by the loosening of the internal motions upon electron attachment, but entropy changes much larger than 10 J K<sup>-1</sup> mol<sup>-1</sup> are reported only for molecules like C<sub>6</sub>F<sub>6</sub> or SF<sub>6</sub> where there may be large differences in symmetry or in geometry between the molecule and the radical anion.<sup>52</sup> Upon the assumption that the entropy change for reaction 3 is about 10 J mol<sup>-1</sup> K<sup>-1</sup>, the EA (≈ -Δ*H*<sup>o</sup> for reaction 3) can be estimated to be 55 ± 5 kJ mol<sup>-1</sup>.

(51) Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem. Phys. Lett.* 1989, 164, 449-454.

(52) Entropy changes upon electron attachment are discussed in ref 6 and ref 52a, b. (a) Chowdhury, S.; Heinis, T.; Grimsrud, E. P.; Kebarle, P. *J. Phys. Chem.* 1986, 90, 2747-2752. (b) Chowdhury, S.; Grimsrud, E. P.; Heinis, T.; Kebarle, P. *J. Am. Chem. Soc.* 1986, 108, 3630-3635.

**Table IV. Thermochemical Data Obtained in the Present Study (values in kJ mol<sup>-1</sup>)**

Δ <i>H</i> <sub>acid</sub> <sup>o</sup> (PhNNHPh)	1465 ± 7
Δ <i>H</i> <sub>acid</sub> <sup>o</sup> (PhNHNHPh)	1514 ± 19
EA(PhN=NPh)	55 ± 5
EA(PhNNHPh) <sup>a</sup>	104
Δ <i>H</i> <sub>f</sub> <sup>o</sup> (PhNNPh) <sup>a</sup>	349
Δ <i>H</i> <sub>f</sub> <sup>o</sup> (PhNNHPh) <sup>a</sup>	310
Δ <i>H</i> <sub>f</sub> <sup>o</sup> (PhNHNHPh) <sup>a</sup>	414
N-H BDE(PhNHNHPh) <sup>a</sup>	306
N-H BDE(PhNNHPh) <sup>a</sup>	208

<sup>a</sup> Estimated from the measured gas-phase acidity of the PhNNHPh and PhNHNHPh species and the obtained EA of azobenzene. The uncertainty on the values may be as large as 19 kJ mol<sup>-1</sup>.

**Reactivity.** The results for reactions of the PhNNPh and PhNNHPh ions with selected molecules are given in Table III together with the structure of the products ions. Neither of the ions reacts with methyl formate, whereas only the radical anion proved unreactive toward CF<sub>3</sub>C-O<sub>2</sub>C<sub>2</sub>H<sub>5</sub>. With CHBr<sub>3</sub>, reaction leads to Br<sup>-</sup> ions in both cases. Proton abstraction is also observed for the PhNNHPh ion (Δ*H*<sub>acid</sub><sup>o</sup> = 1514 ± 19 kJ mol<sup>-1</sup>, see Acidities), indicating that bromoform is more acidic in the gas phase than hydrazobenzene and that the reported value (1546 ± 34 kJ mol<sup>-1</sup>)<sup>53</sup> should be considered as an upper limit to the gas-phase acidity of CHBr<sub>3</sub>. Electron transfer is the only pathway open when the radical anion reacts with C<sub>6</sub>F<sub>6</sub> (Table III) but is not occurring with PhNNHPh as reactant ion. Instead, products are formed that arise from nucleophilic aromatic substitution followed to some extent by fragmentation of the initial product ions.<sup>54</sup> The reactions of the ions with the derivatives of trifluoroacetic acid (Table III) will be discussed in later sections along with the outcome of reactions of the azobenzene radical anion with halogen-substituted methanes.

## Discussion

**Thermochemistry.** The gas-phase acidity of an acid, HA, can be written as shown in eq 4, where BDE(HA) denotes the bond dissociation energy (eq 5) and IE(H) the ionization energy of the hydrogen atom. The determined

$$\Delta H_{\text{acid}}^\circ(\text{HA}) = \text{BDE}(\text{HA}) - \text{EA}(\text{A}^\bullet) + \text{IE}(\text{H}) \quad (4)$$

$$\text{BDE}(\text{HA}) = \Delta H_f^\circ(\text{A}^\bullet) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{HA}) \quad (5)$$

gas-phase acidity of PhNNHPh leads in combination with the measured EA of azobenzene to the homolytic N-H bond energy of the radical of 208 kJ mol<sup>-1</sup>. Subsequently, the N-H BDE of PhNHNHPh is estimated to be 306 kJ mol<sup>-1</sup> on the basis of Δ*H*<sub>f</sub><sup>o</sup>(PhNNHPh) = 414 kJ mol<sup>-1</sup> obtained from eq 5 and the known heat of formation of hydrazobenzene.<sup>55</sup> The experimentally determined thermochemical parameters together with the estimated ones are collected in Table IV.

Bond dissociation energies for the N-H bonds in hydrazines are nearly absent from the literature. For the simplest hydrazine, H<sub>2</sub>NNH<sub>2</sub>, the N-H BDE has been estimated recently to be about 366 kJ mol<sup>-1</sup>,<sup>56</sup> which is 48 kJ mol<sup>-1</sup> larger than an earlier value.<sup>57</sup> On the basis of

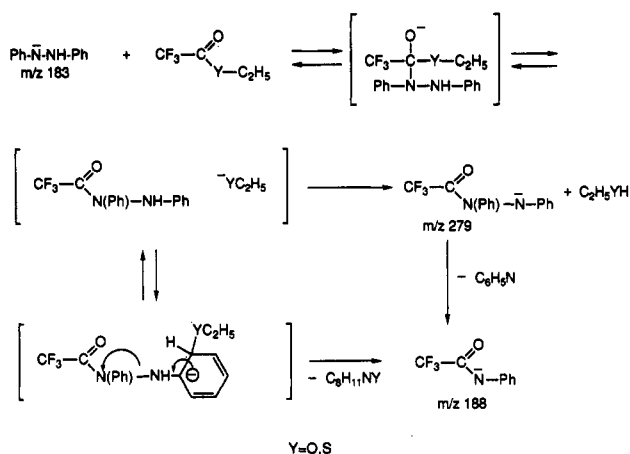
(53) Page, P.; Goode, G. C. *Negative Ions and the Magnetron*; Wiley: New York, 1969.

(54) Nucleophilic aromatic substitution of fluorine-substituted compounds in the gas phase is discussed in ref 54a-c. (a) Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* 1982, 104, 6520-6527. (b) Ingemann, S.; Nibbering, N. M. M. *J. Org. Chem.* 1983, 48, 183-191. (c) Ingemann, S.; Nibbering, N. M. M. *Nouv. J. Chim.* 1984, 8, 299-304.

(55) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(56) Grella, M. A.; Colussi, A. *J. Int. J. Chem. Kinet.* 1988, 20, 713-718.

Scheme I



the recent value,<sup>56</sup> the increase in N-H BDE from hydrazobenzene to hydrazine is 60 kJ mol<sup>-1</sup> and thus is similar to the increase in N-H BDE of 61–81 kJ mol<sup>-1</sup> when going from PhNH<sub>2</sub> to NH<sub>3</sub>.<sup>58</sup> This indicates that the stabilizing influence of the phenyl group on the radical center is comparable for the PhNNHPh and PhNH radicals.

The difference in the first and second N-H BDE of hydrazobenzene of 98 kJ mol<sup>-1</sup> (Table IV) can be used as an estimate of the strength of the  $\pi$ -bond between the nitrogen atoms in azobenzene.<sup>59</sup> We are not aware of previous estimates of the  $-\text{N}=\text{N}-$   $\pi$ -bond energy of azobenzene, but it has been proposed that the strength of  $\pi$ -bonds in an unsaturated system should be comparable in magnitude to the energy barrier for conversion of the *cis* isomer to the *trans* isomer since the bond is broken during the process (see quotation in ref. 59). In line with this suggestion, it can be noted that the present approximate estimate of 98 kJ mol<sup>-1</sup> of the  $\pi$ -bond energy of azobenzene is close to the reported enthalpy barrier of 115 kJ mol<sup>-1</sup> for conversion of *cis*-azobenzene to *trans*-azobenzene in the gas phase.<sup>60</sup>

The lower gas-phase acidity of PhNNHPh than PhNHNHPh can now be traced back to differences in the appropriate N-H bond energies and in the EA values for azobenzene and the PhNNHPh radical (eq 4 and Table IV). The decrease in N-H BDE when going from PhNHNHPh to the radical would lead to a difference in gas-phase acidity of 98 kJ mol<sup>-1</sup>. This variation in BDE is partly compensated by the lower EA of azobenzene than of PhNNHPh (Table IV), and as a result the acidity difference becomes about 49 kJ mol<sup>-1</sup> in the gas phase. In solution, the observed basicity of the conjugate bases is determined in part by the properties of the ions themselves and in part by their interactions with solvent molecules and with counterions. The radical anion can be expected to interact less strongly with the solvent molecules and the counterions than the PhNNHPh ion due to the greater charge localization in the latter. The difference in proton

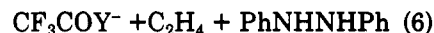
Table V. Product Ions Formed in the Reactions of the PhNNHPh Ion with Halogen-Substituted Methanes and Thermochemical Data for Dissociative Electron Transfer<sup>a</sup>

compd	EA, <sup>b</sup> kJ mol <sup>-1</sup>	product ion (rel intensity)	$\Delta H_r^{\circ}$ , <sup>c</sup> kJ mol <sup>-1</sup>	$T\Delta S_r^{\circ}$ , <sup>c</sup> kJ mol <sup>-1</sup>	$\Delta G_r^{\circ}$ , kJ mol <sup>-1</sup>
CH <sub>3</sub> Cl	-330	no reaction	57	31	26
CH <sub>2</sub> Cl <sub>2</sub>	-120	no reaction	39	32	7
CHCl <sub>3</sub>	-35	Cl <sup>-</sup>	24	35	-9
CCl <sub>4</sub>	>0	Cl <sup>-</sup>	-1	39	-40
CH <sub>3</sub> Br	-45	no reaction	25	31	-6
CH <sub>2</sub> Br <sub>2</sub>		Br <sup>-</sup>	16	33	-17
CHBr <sub>3</sub>		Br <sup>-</sup>	4	38	-34
CBr <sub>4</sub>	(100-200)	Br <sup>-</sup> (70) CBr <sub>4</sub> <sup>-•</sup> (30)	-37	41	-78
CCl <sub>3</sub> Br		Cl <sup>-</sup> (20) Br <sup>-</sup> (80)	-40		

<sup>a</sup> See text. <sup>b</sup> Values from refs 8 and 67. <sup>c</sup> Estimated from data determined in this study and data taken from refs 42, 59, and 68.

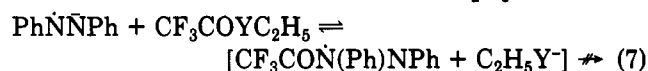
affinity is large enough, however, to cause a lower solution-phase basicity of the radical anion than of the PhNNHPh ion.<sup>29</sup>

**Reactivity.** The PhNNHPh ion reacts with the CF<sub>3</sub>COYC<sub>2</sub>H<sub>5</sub> (Y = O, S) compounds in part by E2 elimination (eq 6) and in part by nucleophilic attack on the carbonyl CF<sub>3</sub>COYC<sub>2</sub>H<sub>5</sub> + PhNNHPh →



group (Table III).<sup>61</sup> The latter process leads to the ion/molecule complex shown in Scheme I which does not dissociate under formation of C<sub>2</sub>H<sub>5</sub>Y<sup>-</sup> ions. Instead, the product ions arise by proton abstraction from the N-H group in the neutral part of the complex followed to some extent by cleavage of the nitrogen-nitrogen bond. Alternatively, the CF<sub>3</sub>CONPh ion may be formed as a result of nucleophilic attack by the C<sub>2</sub>H<sub>5</sub>Y<sup>-</sup> ions on the phenyl ring attached to the N-H group as depicted in Scheme I.

The radical anion of azobenzene does not react with CF<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> and with the sulfur analogue only E2 elimination occurs (Table III). The charge-delocalized radical anion may not be sufficiently reactive to displace the C<sub>2</sub>H<sub>5</sub>Y<sup>-</sup> ions in the reactions with the CF<sub>3</sub>COYC<sub>2</sub>H<sub>5</sub> substrates or the complex shown in eq 7 prefers regeneration of the reactants over dissociation into C<sub>2</sub>H<sub>5</sub>Y<sup>-</sup> ions.



Nucleophilic attack on one of the carbonyl groups in (CF<sub>3</sub>CO)<sub>2</sub>O is observed for the PhNNHPh ion as well as the radical anion. With this substrate, dissociation of the formed ion/molecule complexes into CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> ions is apparently possible for both ions and the preferred pathway for the PhNNHPh ion since only 5% of the product ions arise by proton abstraction within the formed complex (Table III and Scheme I). In conclusion, the difference in reactivity of the two ions can be accounted for by the lower PA of the radical anion than of the PhNNHPh ion and the presence of a N-H group in the latter, which becomes an acidic position in the neutral formed by nucleophilic attack on the carbonyl group in the derivatives of trifluoroacetic acid.

The results for the reactions of the azobenzene radical anion with halogen-substituted methanes are collected in Table V. In principle, the reaction with these substrates can proceed by a S<sub>N</sub>2 substitution or by dissociative

(57) Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* 1958, 29, 442-443.

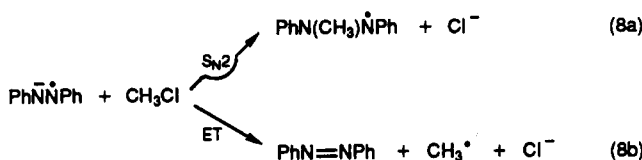
(58) The difference in the accepted values of the N-H BDE of NH<sub>3</sub> (449 kJ mol<sup>-1</sup>) and PhNH<sub>2</sub> (368 kJ mol<sup>-1</sup>) is 81 kJ mol<sup>-1</sup> (values from ref 42). The N-H BDE of PhNH<sub>2</sub> has been reported, however, to be 388 kJ mol<sup>-1</sup>: Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* 1984, 88, 5285-5290. See also: Bordwell, F. G.; Cheng, J. P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* 1988, 110, 1229-1231.

(59) This approach follows the definition of the strength of  $\pi$ -bonds as suggested in Benson, S. W. *Thermochemical Kinetics*, 2nd ed., John Wiley: New York, 1976; pp 63-65.

(60) Andersson, J. A.; Petterson, R.; Tegner, L. *J. Photochem.* 1982, 20, 17-32.

(61) Mechanistic aspects of gas-phase negative ion/molecule reactions are discussed in ref 61a,b. (a) Riveros, J. M.; Jose, S. M.; Takashima, K. *Adv. Phys. Org. Chem.* 1985, 21, 197-241. (b) Nibbering, N. M. M. *Adv. Phys. Org. Chem.* 1988, 24, 1-55.

electron transfer as illustrated for  $\text{CH}_3\text{Cl}$  in eq 8.<sup>62</sup> The



$\text{S}_{\text{N}}2$  substitution is estimated to be exothermic by about  $85 \text{ kJ mol}^{-1}$  for  $\text{CH}_3\text{Cl}$  and by about  $115 \text{ kJ mol}^{-1}$  for  $\text{CH}_3\text{Br}$ .<sup>63</sup> The absence of product ion formation for these typical  $\text{S}_{\text{N}}2$  substrates is in agreement with reports that document the existence of local energy barriers toward exothermic nucleophilic substitution reactions in the gas phase.<sup>64</sup> The electron-transfer pathway is associated with an increase in entropy, but the change is not sufficient to render this pathway thermochemically feasible for the radical anion and  $\text{CH}_3\text{Cl}$  in the gas phase ( $\Delta G^\circ \approx 26 \text{ kJ mol}^{-1}$  for 8b, see Table V).

The reactivity of halogen-substituted methanes as  $\text{S}_{\text{N}}2$  substrates decreases in solution with the introduction of an increasing number of halogen atoms,<sup>65</sup> and a similar trend may hold for the gas phase. Dissociative attachment of free electrons with low kinetic energies is known to become more effective in the gas phase in the order  $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$ ,<sup>66</sup> and it can be expected, therefore, that electron transfer will be the preferred pathway in the reactions of the azobenzene radical anion

(62) The interplay between  $\text{S}_{\text{N}}2$  and electron transfer is discussed in ref 3 and, for example ref 62a-f. (a) Andrieux, C. P.; Gallardo, I.; Saveant, J. M.; Su, K. B. *J. Am. Chem. Soc.* 1986, 108, 638-647. (b) Lund, T.; Lund, H. *Acta Chem. Scand.* 1986, B40, 470-485. (c) Saveant, J. M. *J. Am. Chem. Soc.* 1987, 109, 6788-6795. (d) Lexa, D.; Saveant, J. M.; Su, K. B.; Wang, J. *J. Am. Chem. Soc.* 1988, 110, 7617-7625. (e) Bordwell, F. G.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* 1989, 111, 1052-1057. (f) Ebersson, L.; Shaik, S. S. *J. Am. Chem. Soc.* 1990, 112, 4484-4489.

(63) Based upon the assumption that the N-H BDE of  $\text{PhN}(\text{CH}_3)\text{NPh}$  is the same as for hydrazobenzene, which leads to a  $\Delta H_f^\circ(\text{PhN}(\text{CH}_3)\text{NPh}) = 410 \text{ kJ mol}^{-1}$ .

(64) See, for example: (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* 1983, 105, 2672-2680. (b) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* 1984, 106, 959-966. (c) Bohme, D. K.; Raksit, A. B. *J. Am. Chem. Soc.* 1984, 106, 3447-3452.

(65) Hine, J.; Ehrenson, S. J.; Brader, W. H., Jr. *J. Am. Chem. Soc.* 1956, 78, 2282-2284, and references cited therein.

(66) Christophorou, L. G.; McCorkle, D. L.; Christodoulides, A. A. In *Electron-Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic Press: New York, 1984, Vol. 1, Chapter 6.

with substrates that contain several halogen atoms. From the results in Table V it can be seen that dissociative electron transfer is exoergic for all substrates where  $\text{Cl}^-$  or  $\text{Br}^-$  ions are formed. Thermochemical feasibility is not a sufficient criterion in assigning electron transfer as the mechanism of the reaction leading to  $\text{Cl}^-$  and  $\text{Br}^-$  ions. However, the absence of reaction with  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ , the formation of both  $\text{Cl}^-$  and  $\text{Br}^-$  with  $\text{CCl}_3\text{Br}$  as the substrate, and the formation of a stable  $\text{CBr}_4^{\cdot-}$  ion (Table V) provide evidence that the azobenzene radical anion reacts preferably by the electron-transfer pathway with the compounds in Table V.

The approximate estimates of  $\Delta G_r^\circ$  show that dissociative electron transfer to  $\text{CH}_2\text{Cl}_2$  is slightly endoergic ( $\Delta G_r^\circ \approx 7 \text{ kJ mol}^{-1}$ ), and for  $\text{CH}_3\text{Br}$ , the process is somewhat exoergic ( $\Delta G_r^\circ \approx -6 \text{ kJ mol}^{-1}$ ). Both substrates are unreactive toward the radical anion of azobenzene, indicating that the dissociative surface describing the product configuration intersects the surface of the reactant configuration above the energy level of the separated reactants that in the gas phase corresponds to the fixed energy level of the system. In other words, dissociative electron transfer from the azobenzene radical anion can be associated with a kinetic barrier. The height of the energy barrier toward the reaction can be expected to depend on the difference in EA of the neutral precursor of the reactant radical anion and the EA of the halogen-substituted methane. Although reliable EA (vertical or adiabatic) values for halogen-substituted methanes have not been reported, we conclude from the approximate values listed in Table V<sup>67</sup> and from the absence of reaction with  $\text{CH}_3\text{Br}$  ( $\text{EA} \approx -45 \text{ kJ mol}^{-1}$ ) that dissociative electron transfer from the azobenzene radical anion is possible only when the EA of the halo-methane is larger than  $-45 \text{ kJ mol}^{-1}$ .

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(67) Luke, B. T.; Loew, G. H.; McLean, A. D. *J. Am. Chem. Soc.* 1988, 110, 3396-3400.

(68) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* 1988, 110, 7343-7345.