

Figure 2. Molecular orbital diagram for II. The diagram for I is essentially the same except for the one-electron energies.

at 1.61 ppm in toluene- d_6 . The magnetic susceptibility of I (as a pure solid) has been determined for three independently prepared samples (including the sample from which the crystal for the structure determination was selected),⁷ and the data give an effective magnetic moment, μ_{eff} , of $2.5 \pm 0.1 \mu_B$, independent of temperature in the range 50–300 K. A consideration of the symmetry of the molecule leads to the expectation that I would have a triplet ground state due to a half-filled, doubly degenerate HOMO derived from overlap of the Fe (d_{xz} , d_{yz}) orbitals. A Fenske–Hall⁸ molecular orbital calculation for II gives the one-electron energy level diagram shown in Figure 2 where the HOMO is the π^* orbital derived principally from the interaction of the Fe (d_{xz} , d_{yz}) orbitals. A similar diagram would be expected for I,⁹ except the levels will be somewhat destabilized due to the extra electron density associated with 10 methyl groups. No EPR signal can be found for alkane solutions of I in the temperature range 100–300 K. The μ_{eff} declines somewhat below 50 K, $\mu_{\text{eff}} = 2.36$ at 10 K, indicating a zero field splitting of the triplet state. This is consistent with the absence of an EPR signal.

In the left-most column of Figure 2, the $e_2(\delta\delta)$, $a_1(d\sigma)$, $e_1(d\pi)$, and $a_1(sd\sigma)$ hybrid metal-based frontier orbitals of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ fragment are shown. These are combined into frontier orbitals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]_2$ resulting most notably in $a_1'(\sigma)$, $a_2''(\sigma^*)$, $e_1'(\pi)$, $e_1''(\pi^*)$, and four essentially nonbonding δ levels. When these orbitals are allowed to interact with three CO molecules symmetrically disposed about the Fe–Fe bond, the σ and π orbitals are destabilized through interaction with the CO 5σ orbitals; the σ^* and π^* orbitals are stabilized via donation into the empty 2π orbitals of the CO ligands. The resulting occupied MO's of II,

labeled according to the D_{3h} symmetry of the $\text{Fe}_2(\mu\text{-CO})_3$ core, are $a_1'(\sigma)$, $a_2''(\sigma^*)$, $e' + e''$ (δ nonbonding), and $e''(\pi^*)$ orbitals, the last of which being half-occupied with two electrons results in a triplet ground state. Thus, the HOMO is π^* with respect to the Fe–Fe interaction. The isostructural analogue of I, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_3$,⁶ which has 30 e^- , is diamagnetic.

The electronic structure of I and II closely resembles that of the diamagnetic triplet-decker Fe sandwiches $\text{Fe}_2(\text{CO})_9$ and $(\eta^4\text{-C}_4\text{R}_4)_2\text{Fe}_2(\mu\text{-CO})_3$ ¹¹ which have been analyzed by Hoffmann and co-workers.^{11,12} It is notable that these latter two systems are 34- and 30- e^- systems, respectively, whereas I and II are 32- e^- systems formally isovalent with $\text{Fe}_2(\text{CO})_9$.²⁺ The removal of two weakly Fe–Fe antibonding electrons together with a higher formal Fe oxidation state most likely account for the appreciably shorter (~ 0.26 Å) Fe–Fe bond in I compared to $\text{Fe}_2(\text{CO})_9$.¹³ It is noteworthy that $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-NO})_2$ is reportedly diamagnetic;¹⁴ though isoelectronic with I with II the symmetry¹⁵ of the $\text{Fe}_2(\mu\text{-NO})_2$ core is such that the HOMO is not expected to be 2-fold degenerate.

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Registry No. I, 87985-71-5; II, 87985-70-4; $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$, 35344-11-7; $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}(\text{CO})_2\text{H}$, 80409-91-2.

Supplementary Material Available: Tables I and II giving final positional and thermal parameters and final observed and calculated structure factors for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ (14 pages). Ordering information is given on any current masthead page.

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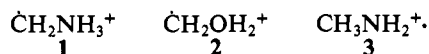
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Reactions of Cyclic Cation Radicals with Nucleophiles: A New Route to Distonic Ions

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Distonic ions¹ such as those represented as **1** and **2** are intriguing



species because often they have no stable neutral counterpart. Ions adopting the distonic form, **1**, have been predicted to be surprisingly more stable than the corresponding conventional isomer, e.g., **3**.² The predicted existence of distonic ions has been confirmed recently in a number of experimental studies.^{3,4}

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(7) The magnetic susceptibility was recorded from 10 to 298 K with pure I loaded in the sample container under an inert atmosphere. After the measurement, the sample was recovered, dissolved in O_2 -, H_2O -free hydrocarbon and reacted with CO to generate $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$. The solvent was removed, the solid was isolated, and the magnetic susceptibility was recorded as a control for possible paramagnetic impurity in I and to establish the diamagnetic correction.

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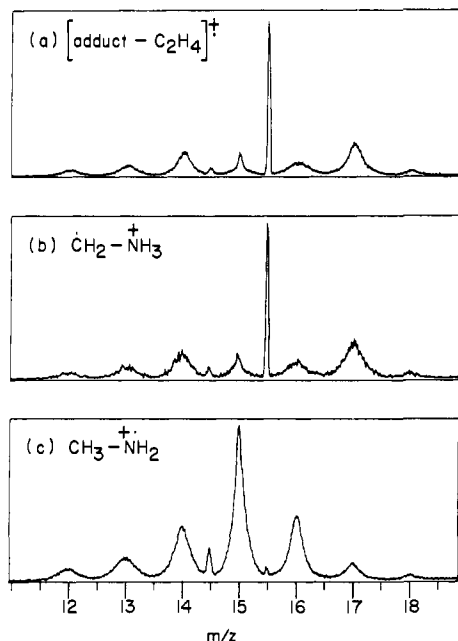
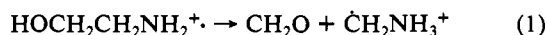
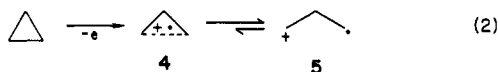


Figure 1. Partial CAD spectra of CH_5N^+ ions derived from (a) the reaction of cyclopropane radical cation and ammonia, (b) the loss of CH_2O from ethanolamine radical cation, and (c) ionization of methylamine.

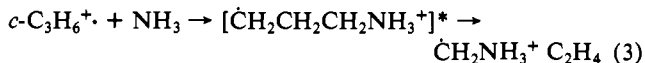
Because distonic cation radicals have no stable neutral precursors, they have been generated by suitable rearrangement or other decomposition reactions which are conveniently conducted in the ion sources of mass spectrometers. The most common route of production is by rearrangement of H and loss of a small neutral molecule such as CH_2O , CO , etc. (eq 1).



We present here evidence for another means to prepare distonic ions which, if general, will provide ready access to a variety of these ions. The route involves the reaction of incipient distonic ions, such as a cycloalkane cation radical, with a nucleophile such as ammonia. Electron ionization of cyclopropane may be viewed to produce a one-electron, long-bonded structure **4**, which in the limit of high vibrational excitation is distonic, **5** (eq 2).^{5,6}



The reaction of cyclopropane cation radical with neutral ammonia leads principally to CH_2NH_2^+ (m/z 30). This reaction has been subjected to detailed study since its discovery in 1971.⁷ A less noticed product is the transient $[\text{CH}_5\text{N}]^+$, m/z 31, which rapidly reacts away in the presence of excess ammonia to give NH_4^+ .⁸



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Table I. CAD Spectra of $\text{C}_3\text{H}_5\text{N}^+$.^a

m/z	precursor	
	adduct	<i>n</i> -propylamine
57	1.9	0.9
56	4.1	2.3
54	1.2	0.7
45	1.0	0.4
44	0.2	0.6
43	2.4	1.2
42	6.4	2.8
41	12.3	7.1
40	2.4	1.0
39	10.8	5.3
38	2.4	1.1
31	5.3	3.7
30	35.9	62.6
29	1.7	1.5
28	3.9	3.3
27	2.4	2.0
26	1.2	0.9
18	2.9	1.5
17	1.0	0.4
15	0.5	0.2

^a Expressed as % total ion abundance. RSD = $\pm 10\%$.

A likely mechanism for production of m/z 31 (eq 3) points to straightforward formation of a distonic ion. By carrying out the reaction in a high pressure source of a tandem mass spectrometer,⁹ a sufficient quantity of m/z 31 can be isolated and collisionally activated and a spectrum of its daughter ions taken.¹⁰ The collisionally activated decomposition (CAD) spectrum is identical with that of authentic CH_2NH_3^+ , produced as in eq 1, and clearly distinct from the CAD spectrum of $[\text{CH}_3\text{NH}_2]^+$ (see Figure 1).

The reaction represents not only an entry to more standard distonic ions such as **1** but also a potential route to others having greater separation of charge and radical sites. The intermediate produced in the reaction depicted as eq 3 is such an example.¹¹ Unfortunately, if the reaction is conducted at the low pressures characteristic of a Fourier transform mass spectrometer cell, no adduct between ammonia and the cyclopropane cation radical can be observed. The excess energy released as new bonds form causes the adduct to decompose to m/z 42, 31, and 30.

However, the adduct can be collisionally stabilized and isolated in a CI source containing a 1:1:0 mixture of cyclopropane, ammonia, and hexafluorobenzene (used as a charge exchange reagent and bath gas) at a total pressure of ca. 300 mtorr. This experimental strategy has proven to be effective for isolating a number of other ion-molecule reaction intermediates.¹² Collisional activation¹⁰ gave a spectrum of fragments that is qualitatively the same as but quantitatively different than that of *n*-propylamine (see Table I). The adduct shows a distinct preference to de-

(8) This CH_5N^+ ion was detected in the original studies of this reaction (see ref 6 a,b) and was observed to react with ammonia faster than CH_3N^+ derived from methylamine. At that time, the structure of CH_5N^+ was speculated to be the distonic ion **1**, on the basis of its enhanced reactivity, but no direct evidence of the distonic structure has ever been presented until now.

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(11) Recent theoretical calculations of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$ show that it is 31 kJ mol⁻¹ more stable than $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2^+$: Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831–1842.

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compose by loss of ammonia and give back the starting $C_3H_6^+$ and its subsequent decomposition products $C_3H_5^+$ and $C_3H_3^+$. The dominant decomposition to $CH_2NH_2^+$ is expected for the distonic ion but it may also signal that the adduct exists as a mixture of the distonic form (see eq 3) and $[n-C_3H_7NH_2]^+$, as has been suggested elsewhere.¹³

In summary, reaction of the cyclopropane cation radical with the nucleophile ammonia produces a new distonic cation radical $\cdot CH_2CH_2CH_2NH_3^+$ which decomposes to $CH_2NH_2^+$ and to another distonic species, $CH_2NH_3^+$. The generality of this route to distonic ions is now under investigation. Encouragement is offered by reports of the reactivity of other small cyclic cation radicals with nucleophiles.^{7,14}

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Registry No. 4, 34496-93-0; NH_3 , 7664-41-7; $\cdot CH_2CH_2CH_2NH_3^+$, 20694-02-4; $\cdot CH_2NH_3^+$, 21444-88-2; $CH_2NH_2^+$, 54088-53-8; $[n-C_3H_7NH_2]^+$, 70677-54-2; $C_3H_8N^+$, 52018-43-6; cyclopropane, 75-19-4; propylamine, 107-10-8.

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Proton-Transfer Spectroscopy of Bis[2,5-(2-benzoxazolyl)]hydroquinone in Supersonic Jets: Effect of van der Waals Complexation with Noble Gas Atoms

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Recently we reported on the dual fluorescence of bis[2,5-(2-benzoxazolyl)]hydroquinone (BBXHQ, Figure 1 inset) in a supersonic free jet.¹ The dual, red and blue, fluorescence is caused by excited-state intramolecular proton transfer (ESIPT).^{2,3} This paper presents novel observations on the effect of complexation with noble gas atoms on the dual fluorescence of BBXHQ.

The first few bands for excitation of red and blue emission from cold, isolated BBXHQ are shown in Figure 1. Excitation at 4178.1 Å gives blue fluorescence; proton transfer also results in a red fluorescence component. The red to blue fluorescence ratio is greatly reversed for bands at 4175.1 and 4184.7 Å. Several distinct ground-state conformers may, in principle, be present in the jet. However, only the dominant band at 4178.1 Å (and hence only one conformer) shall be discussed here. This band can be assigned to the energetically favored conformer having two $OH \cdots N$ hydrogen bonds as shown in Figure 1. Briefly, the reasons⁴ are the

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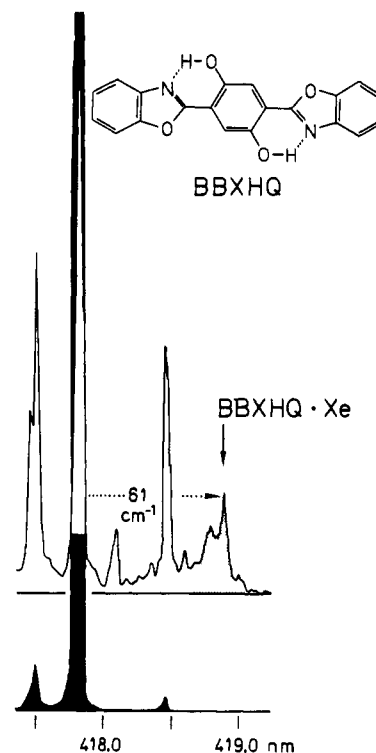


Figure 1. Excitation spectra of BBXHQ in a pulsed supersonic expansion of 6% Xe in He monitoring red (line) and blue fluorescence (solid black). The bands for BBXHQ·Xe are shaded and the microscopic solvent shift is indicated.

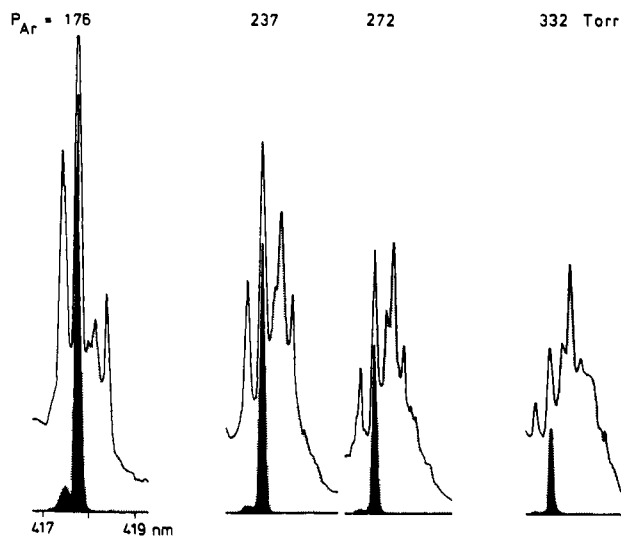


Figure 2. Excitation spectra of BBXHQ in a continuous supersonic expansion of Ar monitoring red (line) and blue fluorescence (solid black). The broadened band due to excitation of BBXHQ·Ar has been shaded.

following: (1) other conformers should have electronic origin transitions at considerably higher energy;⁵ (2) the total emission obtained from excitation at 4178.1 Å is stronger than that of nearby bands; (3) H/D exchange shows two successive blue-shifts for this band, by 57 cm^{-1} each, indicating two equivalent strong hydrogen bonds.⁶

The effect of van der Waals complexation of BBXHQ in a continuous expansion of argon is shown in Figure 2. With increasing stagnation pressure, the sharp bands of the bare molecule decrease. A broadened new band appears at 4182.1 Å

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