# Incorporation of 2-Arylhexa-1,5-diene into Pentasil Zeolite: A Distorted 1-Arylcyclohexane-1,4-diyl Radical Cation at Room Temperature

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Incorporation into a redox-active pentasil zeolite [(Na,H)-ZSM-5] converted 2-arylhexa-1,5-dienes (**9a-c**; aryl = phenyl, tolyl, anisyl) into 1-arylcyclohexane-1,4-diyl radical cations, **10a-c**<sup>++</sup>. The ESR spectra of **10a-c**<sup>++</sup> (six lines, g = 2.0026; a = 9.0 G) indicated the presence of five essentially equivalent nuclei, indicating limited delocalization of spin and charge into the phenyl group. Sequestered in the pores of ZSM-5, the three species **10a-c**<sup>++</sup> are stable at room temperature, in striking contrast to the parent radical cation in cryogenic matrices: cyclohexane-1,4-diyl radical cation is converted to cyclohexene radical cation above 90 K. The structures of radical cation **10a**<sup>++</sup> (X = H) and of the unsubstituted parent were probed by density functional theory (DFT) and ab initio calculations.

# Introduction

One-electron oxidation converts hexadiene systems to a family of interesting radical cation intermediates, which are related to three mechanistic extremes of the Cope rearrangement. Possible pathways include a dissociative, an associative, and a concerted mechanism; radical cation structures representing all three mechanisms have been characterized. For example, one-electron oxidation of dicyclopentaliene vields radical cation.  $1^{++}$ . a species containing two noninteracting allyl functions. In this species the cleavage of C-3-C-4 is complete, whereas bond formation between C-1 and C-6 has not begun.<sup>1</sup> Similar oxidation of tricyclooctadienes (2, X = -, C=O, CH<sub>2</sub>) generates radical cations, 2<sup>•+</sup>, containing two allyl groups in close contact: addition and cleavage have proceeded to a similar degree (in "concert").<sup>2</sup> Finally, radiolysis of 1,5-hexadiene in cryogenic matrices gives rise to cyclohexane-1,4-diyl radical cation,  $3^{+}$ , in which C-1-C-6-addition is complete without significant weakening of the C-3-C-4-bond.<sup>3</sup> These structures illustrate remarkable differences between the potential surfaces of radical cations and neutral precursors: states of intermediate geometry are minima on the radical cation potential surface but saddle points (transition structures) on the parent potential surface. In essence, the parent molecules undergo concerted Cope rearrangements via a transition structure,<sup>4</sup> whereas the cycloaddition or cleavage of the radical cations is "arrested" at intermediate geometries.



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Chemical evidence for substituted radical cations of the cyclohexane-1,4-diyl structure type was obtained in solution during the electron transfer initiated photoreaction of 2,5diarylhexa-1,5-dienes, 4, by the distribution of a deuterium label between the terminal olefinic (C-1, C-6-) and the allylic (C-3, C-4-) positions.<sup>3b-e</sup> Diarylcyclohexane-1,4-diyl radical cations,  $5^{++}$ , were intercepted by molecular oxygen (O<sub>2</sub>); the structure of the resulting endo-peroxides revealed the steric course of the ring closure. For example, the isomeric 1,4-diaryl-5,6-dimethyl derivatives, 8, obtained from 3,6-diarylocta-2,6-dienes, 6, indicate that  $6^{++}$  generated the chair form,  $7^{++}$ . Accordingly, the ring closure of hexa-1,5-diene radical cations occurs in the same stereospecific manner<sup>3b-e</sup> established for the thermal rearrangement of the neutral parent.<sup>4</sup> The 1,4-diarylcyclohexane-1,4-diyl radical cations exist in the chair form as does the parent radical cation, 3<sup>•+</sup>, in cryogenic matrices.<sup>3a</sup>



It appeared to be of interest to generate radical cations of the hexa-1,5-diene family in a zeolite host to study their behavior confined within the limiting interior. Various organic radical cations can be generated spontaneously by inclusion of their precursors into zeolites.<sup>5,6</sup> The rigid microporous solids stabilize the otherwise highly reactive radical cations due to the

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Incorporation of 2-Arylhexa-1,5-diene into Pentasil Zeolite

SCHEME 1



combined effects of (a) the intense electrostatic fields inside zeolites, (b) topological restrictions that prevent the access of external reagents, and (c) the limiting dimensions of the zeolite channels, which may restrict the shape of the enclosed intermediates.<sup>6,7</sup> Typically, radical cations generated in zeolites have extended lifetimes and can, therefore, be studied by conventional spectroscopic techniques. On the other hand, some radical cations sequestered in zeolites undergo rapid conversions, which are without precedent in cryogenic matrices or in solution.<sup>8</sup> For example, *p*-propylanisole gave rise to *p*-propenylanisole radical cation;<sup>8a</sup> 2-phenyl-1,3-dithiane formed 1,2-dithiolane radical cation;<sup>8b</sup> trans-1,2-diphenylcyclopropane was converted to *exo,exo*-1,3-diphenylallyl radical;<sup>8c</sup> and *p*-cyclopropylanisole gave rise to *p*-propenylanisole radical cation.<sup>8d</sup>

In light of these findings we expected interesting results from the incorporation of hexa-1,5-dienes into appropriate zeolites. We selected 2-aryl-substituted derivatives, 9a-c, because their redox potentials fall into the range that can be oxidized by redox-active acidic pentasil zeolite (H–ZSM-5) or mordenite (H–mor).

### **Experimental Section**

**Materials.** H–ZSM-5 was prepared from synthetic Na–ZSM-5 (hydrothermal crystallization of silica and alumina gels in aqueous NaOH medium)<sup>10</sup> by Na<sup>+</sup>-to-NH<sub>4</sub><sup>+</sup> ion exchange followed by 12 h deep-bed calcination at 500 °C under air. Similarly, H–mor was prepared from commercial NH<sub>4</sub><sup>+</sup>–mor by 12 h calcination at 500 °C and stored in vacuo. Commercial samples of 1-*p*-anisylcyclohex-1-ene, **11a** (Aldrich), and *p*-methoxybiphenyl, **13** (Aldrich), were used as received. Donor molecule **9c** was synthesized from *p*-anisaldehyde, **17c**, by reaction with 4-butenylmagnesium bromide, oxidation of the resulting alcohol, **18c**, with MnO<sub>2</sub>, and Wittig reaction of the resulting ketone, **19c** (Scheme 1).

Donor molecule **12c** was synthesized from cyclohexane-1,4dione mono-ethylene ketal, **20**, by the reaction with *p*-anisyl-



**Figure 1.** (top) X-band EPR generated by sequestering 2-*p*-anisylhexa-1,5-diene, **9c**, into a redox active pentasil zeolite, (Na,H)-ZSM-5. The spectrum is split into a sextet (relative intensities ~1:4:6:6:4:1) due to hyperfine interaction with 5 essentially equivalent <sup>1</sup>H nuclei (a = 9.0 G) and is identified as that of 1-*p*-anisylcyclohexane-1,4-diyl radical cation, **10c**<sup>++</sup>. (bottom) A simulated second-order spectrum consisting of two isotropic spectra (in the ratio of 1:1): a spectrum with g =2.0026 and an isotropic coupling constant, a(5H) = 9.0 G and a Lorentzian spectrum with a line width of 32.0 G.

lithium; acid workup furnished the *p*-anisylcyclohexenone, **21c**. Reduction with sodium borohydride furnished the alcohol, **22c**; finally, the corresponding tosylate, **23c**, was converted to the cyclohexadiene, **12c**, with potassium t.-butoxide in tetrahydro-furan (Scheme 2).

**Incorporation Procedures.** The neutral diamagnetic substrates were incorporated/adsorbed into pentasil zeolite or mordenite by stirring solutions of 10 mg in 15 mL anhydrous 2,2,4-trimethylpentane in the presence of 250 mg thermally (500 °C, 12 h) dehydrated H–ZSM-5 for 30 min at room temperature. The loaded zeolite was collected by filtration and washed with dry *n*-hexane; the solids so obtained were dried at reduced pressure ( $\leq 1$  Torr) for 1 h and stored in closed vials.

**ESR Spectra.** ESR spectra of the dried zeolite samples were recorded on an X-band spectrometer (9.3 GHz) in the CW mode. Typically, a single scan gave a satisfactory spectrum; the spectra reproduced in the figures are accumulations of eight scans.

# **Results and Discussion**

Three arylhexadienes, 2-phenyl- (9a, X = H), 2-tolyl- (9b,  $X = CH_3$ ), or 2-anisylhexa-1,5-dienes (9c,  $X = OCH_3$ ), were incorporated from 2,2,4-trimethylpentane solutions into thermally dehydrated samples of sodium or hydrogen pentasil zeolite [(Na,H)-ZSM-5] or hydrogen mordenite (H-mor). Incorporation into H-ZSM-5 and H-mor caused the colorless suspensions to turn light blue and the zeolite surfaces more intense blue, whereas the Na-ZSM-5 samples showed little or no coloration. After washing and evaporating the solvent, the loaded H-ZSM-5 and H-mor samples showed ESR spectra, assigned to radical cations, 10a-c+, whereas the Na-ZSM-5 samples failed to show any ESR signals with appreciable signal-to-noise ratios  $(\geq 3)$ . Apparently Na–ZSM-5 is not sufficiently redox-active to oxidize the substrates 9a-c. The ESR spectra observed in H-ZSM-5 for  $10a-c^{+}$  show differing signal intensities, the samples prepared from 9c (e.g., Figure 1) being the strongest and those prepared from 9a being weakest; the EPR spectra are persistent at room temperature. The spectrum assigned to



Figure 2. X-band EPR spectra obtained upon sequestering 2-*p*-anisylhexa-1,5-diene, 9c, into (Na,H)-mor (center), and of the same sample after 6 h at room temperature (bottom). Comparison with the spectrum obtained in (Na,H)-ZSM-5 (top) shows that species  $10c^{++}$  is present but decays slowly to a secondary species, assigned to 1-*p*-anisylcyclohexadiene radical cation,  $12c^{++}$  (bottom), by comparison with a spectrum obtained by incorporation of authentic 12c.

**10c**<sup>++</sup> obtained from **9c** (g = 2.0026, a = 9.0 G), indicated the presence of five essentially equivalent nuclei.



The ESR spectra arising from incorporation of **9a-c** into (Na,H)—mor were similar to those obtained in H–ZSM-5; however, they were less clearly defined and had somewhat reduced wing signals (e.g., Figure 2, center, from **9c**). The EPR spectrum of **10c**<sup>++</sup> observed initially in H–mor (Figure 2, center) changed slowly over a period of several hours. The outer (wing) signals of **10c**<sup>++</sup> decayed further, and the overall spectrum was replaced by a secondary spectrum, a poorly resolved multiplet (Figure 2, bottom).

In an attempt to probe the identity of the secondary species observed in H-mor, we incorporated three potential products, 1-*p*-anisylcyclohexene, **11c**, 1-*p*-anisylcyclohexa-1,3-diene, **12c**, and *p*-methoxybiphenyl, **13c**, into H-ZSM-5 and compared the resulting spectra with that spectrum (Figure 2, bottom). These substrates were chosen because results of previous studies suggested that a radical cation of structure **10c**<sup>++</sup> might undergo a combination of deprotonation-oxidation and dehydrogenation-

oxidation in the zeolite interior.<sup>8a,d</sup> The spectra obtained from **11** and **12** were essentially identical, suggesting that  $11^{\bullet+}$  is readily converted to  $12^{\bullet+}$  in the zeolite channels. Because the spectrum of  $12^{\bullet+}$  closely resembled the secondary spectrum in H-mor (Figure 2, bottom), that spectrum was assigned as due to  $12^{\bullet+}$ . Further comparison with the ESR spectrum from the sample prepared from 13c argued against the subsequent conversion of  $12c^{\bullet+}$  to  $13c^{\bullet+}$ .

In addition to the acyclic precursors, 9a-c, we also attempted to generate the 1-arylcyclohexane-1,4-diyl system by allowing 1-anisyl-2,3-diazabicyclo[2.2.2]oct-2-ene, **14c**, to interact with H-ZSM-5. Loss of nitrogen from the potential radical cation, **14c**<sup>•+</sup>, would also give rise to **10c**<sup>•+</sup>. Of course, the rigid structure of this precursor might prevent its incorporation into the zeolite channels. This attempt gave rise to a weak, broad ESR spectrum with essentially no fine structure. The absence of any characteristic <sup>14</sup>N splitting suggested that the spectrum might be due to a deazetized species; obviously **14c** was not converted to **10c**<sup>•+</sup> in the zeolite interior. The broad signal might be due to a species on the external zeolite surface, generated by oxidation or protonation on an appropriate zeolite site.



The six-line spectra (Figure 1, top) obtained from 2-*p*anisylhexa-1,5-diene, **9c**, and from **9a,b** in the zeolite indicate that five <sup>1</sup>H nuclei have equivalent or very similar hyperfine coupling constants (hfcc). Such spectra are formally compatible with the chair conformer of cyclized radical cations, e.g., 1-*p*anisylcyclohexane-1,4-diyl radical cation, **10c**<sup>++</sup>, in which the  $\alpha$ -proton at C-4 and the two pairs of axial  $\beta$ -protons (H<sub>2,6ax</sub> and H<sub>3,5ax</sub>) would interact strongly with the unpaired spin. The generation of **10a**-c<sup>++</sup> from **9a**-c is analogous to the formation of **3**<sup>++</sup> from 1,5-hexadiene in cryogenic matrices,<sup>3a</sup> however, with two significant noteworthy features: the persistence, especially of **10c**<sup>++</sup>, and the unexpected apparent equivalence of the hfccs for the four axial  $\beta$ -protons.

The observation that 10a-c+ are persistent at room temperature is surprising, given that  $3^{++}$  was converted to cyclohexene radical cation above 90 K, by a (1,3-) shift of an axial hydrogen or its mechanistic equivalent.<sup>3a</sup> The persistence of  $10a-c^{+}$  is all the more remarkable, as deprotonations, dehydrogenations, or net hydrogen migrations readily occur in zeolites. For example, oximes readily form iminoxyls,9 p-propylanisole gives rise to p-propenylanisole radical cation,<sup>8a</sup> and p-anisylcyclopropane is converted to 1-p-anisylpropene radical cation.<sup>8d</sup> In light of these results, one might have expected radical cations  $10a-c^{+}$  to rearrange to 1-*p*-arylcyclohexene radical cations,  $11a-c^{+}$ , or be dehydrogenated to 1-*p*-arylcyclohexa-1,3-dienes,  $12a-c^{+}$ , or *p*-substituted biphenyl radical cations, 13a-c\*+. The unexpected stability of 10a-c\*+ in ZSM-5 can be explained if it is generated in an alignment that is unfavorable for deprotonation/dehydrogenation. Thus, the stabilization would be ascribed to the limiting geometry of ZSM-5.

Support for this interpretation is derived from the observation that  $10a-c^{++}$  are indeed dehydrogenated in acidic mordenite, which has larger pores than pentasil zeolite and, thus, allows the sequestered entity greater mobility and flexibility. The EPR spectrum of  $10c^{++}$  observed initially upon incorporation of 9c into H-mor (Figure 2, center) changes slowly over a period of

TABLE 1: C–C Bond Lengths (Å) Calculated for Cyclohexane-1,4-diyl  $(3^{+})$  and 1-Phenyl-cyclohexane-1,4-diyl Radical Cations  $(10c^{+})$ 

				1-Phenylcyclohexane-1,4-diyl							
	Cyclohexane-1,4-diyl			conjugated		rotated 60°		orthogonal <sup>b</sup>		pseudo twist boat	
bond	UMP2	UB3LYP	UB3LYP <sup>c</sup>	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP
$C_1 - C_2$	1.449	1.454	1.451	1.476	1.483	1.449	1.464	1.467	1.464	1.504	1.489
$C_2 - C_3$	1.664	1.672	1.672	1.579	1.614	1.579	1.655	1.669	1.655	1.534	1.553
$C_3 - C_4$	1.449	1.454	1.451	1.485	1.472	1.449	1.461	1.439	1.461	1.436	1.485
$C_4 - C_5$	1.449	1.454	1.451	1.485	1.472	1.49	1.461	1.439	1.461	1.436	1.487
$C_5 - C_6$	1.664	1.672	1.672	1.579	1.614	1.664	1.655	1.660	1.655	1.534	1.540
$C_1 - C_6$	1.449	1.454	1.451	1.476	1.483	1.476	1.464	1.467	1.464	1.404	1.503
$C_1 - C_{1'}$				1.421	1.426	1.430	1.476	1.472	1.476	1.426	1.422

<sup>*a*</sup> Unless otherwise noted, all calculations were carried out with the 6-31G\* basis set. <sup>*b*</sup> Optimized with the phenyl group held rigidly in the plane bisecting the cyclohexanediyl ring system through C1 and C4. <sup>*c*</sup> Calculated with the 6-311G\* basis set.

several hours. The outer (wing) signals of  $10c^{++}$  decay further, and the overall spectrum is replaced by a secondary spectrum (Figure 2, bottom) assigned to 1-*p*-anisylcyclohexa-1,3-diene radical cation,  $12c^{++}$ . This conversion requires the net loss of H<sub>2</sub> or of two electrons and two protons in any sequence or combination. Mechanistic details about this conversion, e.g., whether 1-arylcyclohexene radical cation,  $11^{++}$ , is an intermediate, could not be determined.

The second unexpected finding, that the two pairs of axial  $\beta$ -protons have essentially identical hfccs, requires that the unpaired spin is distributed essentially evenly between the 2p orbitals at C-1 and C-4 and, notably, that the distribution of spin and charge in the radical cation is not significantly affected by the aryl group at one of the spin-bearing centers. The fact that the coupling constant of the five <sup>1</sup>H nuclei is only slightly reduced (9.0 G) relative to those of  $3^{\bullet+}$  (11.9 G)<sup>3a</sup> also seems to suggest limited delocalization of unpaired spin into the anisyl group. Further, the hfccs for the anisyl (as well as the equatorial) protons fall within the line width of the spectrum ( $\sim$ 8.0 G). Although the lines are broad, this width is given by the sum of the hfcs of all these protons. The apparent limited delocalization could be due to rotation of the aryl moiety from the conjugated orientation,  $10^{\bullet+}_{con}$ , into an orthogonal one,  $10^{\bullet+}_{ort}$ . This result, too, could be ascribed to the limiting geometry of the zeolite.



In an attempt to probe this aspect we carried out DFT and ab initio calculations on the 1-phenylcyclohexane-1,4-diyl radical cation,  $10a^{\bullet+}$ , in two limiting orientations,  $10a^{\bullet+}_{con}$  and  $10a^{\bullet+}_{ort}$ ; additional conformers were also considered. For comparison and to calibrate the calculations, the unsubstituted cyclohexane-1,4-diyl radical cation,  $3^{\bullet+}$ , was calculated.

**Computational Details.** Ab initio and density functional theory (DFT) calculations for the radical cations,  $3^{++}$ ,  $10a^{++}_{con}$ , and  $10a^{++}_{ort}$ , were carried out with the Gaussian 03 suite of electronic structure programs<sup>11</sup> using extended basis sets, including p-type polarization functions on carbon. The geometries of the radical cations were optimized at the unrestricted B3LYP<sup>12</sup> level with the standard 6-31G\* basis set. The importance of higher degrees of electron correlation was investigated at the unrestricted MP2<sup>13</sup> level of theory (UMP2/6-31G\*//UMP2/6-31G\*). Vibrational analyses confirmed two DFT stationary points as energy minima (no imaginary frequencies). Wave function analyses for charge and spin density distributions used the conventional Mulliken partitioning scheme.<sup>11</sup> In addition, atomic charges were also calculated using NPA

methodology as incorporated in the NBO program;<sup>14</sup> however, the resulting charge densities provide limited insights (Table 4).

In our experience, Møller–Plesset perturbation theory (MP2) reproduces *positive* <sup>1</sup>H hyperfine coupling constants satisfactorily, but overestimates spin densities on carbon and negative hfcs significantly, in some cases by factors >2.<sup>15</sup> On the other hand, density functional theory methods<sup>16</sup> often give satisfactory agreement<sup>17</sup> with experimental results. Indeed, positive and negative hfcs of norbornadiene,<sup>17a,b</sup> quadricyclane,<sup>17a,b</sup> and bicyclobutane radical cations<sup>17b</sup> are reproduced accurately with both (B3LYP/6-31G\*//MP2/6-31G\*) and (B3LYP/6-31G\*//B3LYP/6-31G\*) methods.<sup>17b</sup>

**Cyclohexane-1,4-diyl Radical Cation.** The radical cation, **3**<sup>+</sup>, has a <sup>2</sup>Y' electronic state and *C<sub>s</sub>* symmetry; the minimization converges to this symmetry if no symmetry is imposed. The carbon skeleton has four shorter [C-1–C-2, C-1–C-6, C-3–C-4, C-4–C-5 = 1.449 Å (UMP2); = 1.454 Å (UB3LYP)] and two "long" C–C bonds [(C-2–C-3, C-5–C-6 = 1.664 Å (UMP2); = 1.672 Å (UB3LYP)]. These bond lengths (Table 1) reflect an intermediate in which the C-3–C-4-bond is partially cleaved and the C-1–C-6-bond is partially formed. The presence of equivalent spin density on C-1 and C-4 supports a delocalized structure. The actual spin densities on these carbons depend on the level of perturbation theory included; they are higher with the MP2 ( $\rho_{1,4} = 0.60$ ) than with the B3LYP method ( $\rho_{1,4} =$ 0.56; Table 2).

Not surprisingly, the structure type derived by considering the unpaired spin density distribution is also fully revealed in the hyperfine coupling pattern. The protons at the sp<sup>2</sup> hybridized carbons, C-1 and C-4, show significant negative hfcs, whereas the two pairs of axial  $\beta$ -protons have sizable positive hfcs; the equatorial  $\beta$ -protons have minor or negligible hfcs  $[|a_{2,3,5,6eq}|]$ < 1.5 G (UMP2); < 0.3 G (UB3LYP)]. The degree of delocalization depends on the level of perturbation theory (Table 3). At the MP2 level, the negative coupling  $(a_{1,4} = -15.2 \text{ G})$ is slightly larger than the positive one  $(a_{2,3,5,6ax} = 12.2 \text{ G})$ , whereas at the B3LYP level the negative and the major positive couplings are more similar ( $a_{1,4} = -12.5$  G;  $a_{2,3,5,6ax} = 13.5$ G). These results are in satisfactory agreement with the experimental values (|a| = 12.0 G).<sup>3a</sup> A calculation using the 6-311G\* basis reduced the negative hfccs but left the positive ones essentially unchanged ( $a_{1,4} = -11.3$  G;  $a_{2,3,5,6ax} = 13.5$ G), widening the mismatch between them. In summary, the UB3LYP calculations reproduce the hyperfine coupling constants and, by inference, the structure of cyclohexane-1,4-diyl radical cation satisfactorily.

1-Phenylcyclohexane-1,4-diyl Radical Cation. Calculating the phenyl-substituted radical cation,  $10a^{++}_{con}$ , proved more

TABLE 2: Mulliken Atomic Spin Densities ( $\rho$ ) Calculated for Cyclohexane-1,4-diyl (3•<sup>+</sup>) and 1-Phenylcyclohexane-1,4-diyl Radical Cations (10c•<sup>+</sup>)<sup>*a*</sup>

				1-Phenylcyclohexane-1,4-diyl								
	Cyclohexane-1,4-diyl			conjugated		rotated 60°		orthogonal <sup>b</sup>		pseudo twist boat		
bond	UMP2	UB3LYP	UB3LYP <sup>c</sup>	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP	
C1	0.596	0.563	0.559	0.221	0.192	0.364	0.320	0.746	0.436	0.789	0.108	
$C_2$	-0.040	-0.031	-0.030	-0.007	0.014	-0.035	-0.002	-0.072	-0.011	0.071	0.003	
$C_3$	-0.040	-0.031	-0.030	-0.082	-0.061	-0.047	-0.052	-0.007	-0.044	0.003	-0.069	
$C_4$	0.596	0.563	0.559	1.061	0.784	0.811	0.712	0.401	0.659	0.010	0.898	
$C_5$	-0.040	-0.031	-0.030	-0.082	-0.061	-0.074	-0.052	-0.007	0.044	0.003	-0.069	
$C_6$	-0.040	-0.031	-0.030	-0.007	0.014	-0.032	-0.084	-0.072	-0.011	0.071	0.005	

<sup>*a*</sup> Unless otherwise noted, all calculations were carried out with the 6-31G\* basis set. <sup>*b*</sup> Optimized with the phenyl group held rigidly in the plane bisecting the cyclohexanediyl ring system through C1 and C4. <sup>*c*</sup> Calculated with the 6-311G\* basis set.

TABLE 3: Calculated Hyperfine Coupling Constants (*a*, G) for Cyclohexane-1,4-diyl ( $3^{+}$ ) and 1-Phenylcyclohexane-1,4-diyl Radical Cations ( $10c^{+}$ )<sup>*a*</sup>

				1-Phenylcyclohexane-1,4-diyl							
	Cyclohexane-1,4-diyl			conjugated		rotated 60°		orthogonal <sup>b</sup>		pseudo twist boat	
proton	UMP2	UB3LYP	UB3LYP <sup>c</sup>	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP	UMP2	UB3LYP
$H_1$	-15.22	-12.45	-11.25								
H <sub>2ax</sub>	12.20	13.47	13.48	2.28	2.79	10.73	8.00	17.7	9.32	28.33	7.61
$H_{2eq}$	-1.47	-0.22	-0.27	0.46	0.14	3.10	-0.21	0.02	-0.14	13.75	-0.54
H <sub>3ax</sub>	12.20	13.47	13.48	37.39	24.05	14.35	18.78	5.68	17.4	-1.07	38.51
$H_{3eq}$	-1.47	-0.22	-0.27	7.48	1.93	-3.07	0.48	-3.00	-0.41	1.17	10.35
$H_4$	-15.22	-12.45	-11.25	-29.92	-18.35	-18.92	-16.11	-7.63	-14.25	-0.43	-21.44
H <sub>5ax</sub>	12.20	13.47	13.48	37.39	24.05	12.59	18.06	5.68	17.4	-1.06	34.29
H <sub>5eq</sub>	-1.47	-0.22	-0.27	7.48	1.93	-4.66	0.37	-3.00	0.41	1.19	30.86
H <sub>6ax</sub>	12.20	13.47	13.48	2.28	2.79	16.28	16.54	17.7	9.32	28.36	-0.88
H <sub>6eq</sub>	-1.47	-0.22	-0.27	0.46	0.14	5.61	0.67	0.02	-0.14	16.68	1.14

<sup>*a*</sup> Unless otherwise noted, all calculations were carried out with the 6-31G\* basis set. <sup>*b*</sup> Optimized with the phenyl group held rigidly in the plane bisecting the cyclohexanediyl ring system through C1 and C4. <sup>*c*</sup> Calculated with the 6-311G\* basis set.

 TABLE 4: Atomic Charges (f) Calculated for Cyclohexane-1,4-diyl (3•<sup>+</sup>) and 1-Phenylcyclohexane-1,4-diyl Radical Cations  $(10c•^+)^a$ 

				1-Phenylcyclohexane-1,4-diyl						
		Cyclohexane-1,4-di	yl	conj	ugated	orthogonal <sup>b</sup>				
atoms	UMP2	UB3LYP	UB3LYP <sup>c</sup>	UMP2	UB3LYP	UMP2	UB3LYP			
$C_1$	0.004	0.009	0.017	0.087	0.154	0.324				
$C_{2,6}$	-0.405	-0.516	-0.349	-0.514	-0.404	-0.517	9.32			
C <sub>3,5</sub>	-0.405	-0.516	-0.349	-0.514	-0.354	-0.501	-0.14			
$C_4$	0.004	0.009	0.017	0.087	-0.137	-0.113	17.4			
$H_1$	0.266	0.263	0.238	0.261			-0.41			
$H_{2,6ax}$	0.254	0.288	0.233	0.290	0.238	0.288	-14.25			
$H_{2,6eq}$	0.266	0.304	0.238	0.300	0.224	0.271				
H <sub>3,5ax</sub>	0.254	0.288	0.233	0.290	0.205	0.258				
H <sub>3,5eq</sub>	0.266	0.304	0.238	0.300	0.233	0.285				
$H_4$	0.266	0.263	0.238	0.261	0.231	0.246				

<sup>*a*</sup> Unless otherwise noted, all calculations were carried out with the  $6-31G^*$  basis set. <sup>*b*</sup> Optimized with the phenyl group held rigidly the plane bisecting the cyclohexandiyl ring system through C1 and C4. <sup>*c*</sup> Calculated with the  $6-311G^*$  basis set.

problematic than the parent,  $3^{\bullet+}$ , because of the increased number of heavy atoms and because of having to impose constraints on the geometry of the phenyl group. The dimensions of the species suggest that it should be readily accommodated in ZSM-5. For this consideration the longest extension, the distance  $l = H_4-H_p = 8.82$  Å, is less important; however, "depth",  $d = H_{2eq}-H_{6eq} = 4.33$  Å, and "height",  $h = H_{2ax}-H_{5ax} = 3.07$  Å, are compatible with the zeolite dimensions (Figure 3).

Given that  $10a^{++}_{con}$  can be accommodated inside pentasil zeolite, we examined its spin density distribution and hyperfine coupling pattern to judge whether they are compatible with the ESR results. Both the UMP2 and UB3LYP methods essentially localized spin and charge in different sections of the species: the positive charge is largely located on the benzyl function whereas the unpaired electron spin resides mainly on C-4 [ $\rho_4$  = 1.06 (UMP2),  $\rho_4$  = 0.78 (UB3LYP)] and it is delocalized unto C-1 only to a limited degree [ $\rho_1$  = 0.22 (UMP2),  $\rho_1$  = 0.19 (UB3LYP), Table 2]. Given this distribution of electron spin density, the hfcc of H-4 and those of the two pairs of axial <sup>1</sup>H nuclei are significantly different, particularly with Møller– Plesset perturbation theory [ $a_4$  = -29.9 G,  $a_{2,6ax}$  = 2.3 G,  $a_{3,5ax}$ = 37.4 G (UMP2);  $a_4$  = -18.4 G,  $a_{2,6ax}$  = 2.8 G,  $a_{3,5ax}$  = 24.1 G (UB3LYP)]. Obviously, this splitting pattern is incompatible with the experimental results.

One possible explanation for the mismatch between calculation and experiment involves a structure in which the zeolite has caused the phenyl group to twist out of conjugation. To evaluate a structure with limited delocalization of spin and charge into the phenyl group, we constructed structure  $10a^{+}_{ort}$ by rotating the phenyl group 90° to position it into the plane bisecting the cyclohexandiyl ring system through C-1 and C-4.



**Figure 3.** (top) The dimensions of the conjugated 1-phenylcyclohexane-1,4-diyl radical cation,  $10a^{++}_{con}$ . (bottom) Docking of  $10a^{++}_{con}$  inside pentasil zeolite viewed along the cylindrical channel axis (right) and perpendicular to it (left).

The relative enthalpy and the relative free energy of  $10a^{++}_{ort}$  at 298.14 K lie 15.4 and 17.9 kcal/mol, respectively, above those of  $10a^{++}_{con}$ . It is hardly surprising that a vibrational analysis (UB3LYP/6-31G\*) shows one imaginary frequency for the structure with enforced  $C_s$  geometry:  $10a^{++}_{ort}$  is not an energy minimum, at least not in the vacuum calculations. An animation of the imaginary frequency shows twisting of the orthogonal phenyl and cyclohexane-1,4-diyl units in the direction toward the conjugated structure,  $10a^{++}_{con}$ . The dimensions of  $10a^{++}_{ort}$  also are compatible with the dimensions of the ZSM-5 channels. Of the dimensions of  $10a^{++}_{ort}$ ,  $l = H_4 - H_p = 8.76$  Å,  $d = H_{3eq} - H_{5eq} = 4.30$  Å, and  $h = H_o - H_{o'} = H_m - H_{m'} = 4.32$  Å, only the "height" is noticeably increased without, however, affecting its compatibility (Figure 4).

The unpaired electron spin density for  $10a^{++}_{ort}$  is more evenly delocalized than for  $10a^{++}_{con}$ ; however, UMP2 and UB3LYP methods show divergent trends. With the UMP2 method the highest spin density is found on C-1 ( $\rho_1 = 0.75$ ,  $\rho_4 = 0.40$ , Table 2), whereas it resides on C-4 with the UB3LYP method ( $\rho_1 = 0.44$ ,  $\rho_4 = 0.66$ ). The calculated hyperfine splittings cover a smaller range than for the conjugated structure [ $a_4 =$ -7.6 G,  $a_{2,6ax} = 17.7$  G,  $a_{3,5ax} = 5.7$  G (UMP2);  $a_4 = -14.3$ G,  $a_{2,6ax} = 9.3$  G,  $a_{3,5ax} = 17.4$  G (UB3LYP), Table 3]. Still, large differences remain between the splittings calculated for the three types of nuclei. Also, the largest hfccs calculated with either UMP2 (17.7 G) or UB3LYP (17.4 G, -14.3 G) are incompatible with the experimental spectra. Accordingly, structure  $10a^{++}_{ort}$  is not a good representation of the species in the zeolite.

The obvious discrepancy between the hyperfine coupling patterns of  $10a^{++}_{ort}$  and  $10a^{++}_{con}$ , respectively, and the experimental results caused us to evaluate additional conformers of  $10a^{++}$ , a pseudo twist boat species,  $10a^{++}_{ptb}$ , as well as structures in which the phenyl group is rotated different degrees from the plane bisecting the cyclohexan-1,4-diyl ring system through C-1 and C-4. The pseudo twist boat form,  $10a^{++}_{ptb}$ , (Figure 5) is a



**Figure 4.** (top) The dimensions of the bisected 1-phenylcyclohexane-1,4-diyl radical cation,  $10a^{*+}_{ort}$ . (bottom) Docking of  $10a^{*+}_{ort}$  inside pentasil zeolite viewed along the cylindrical channel axis (right) and perpendicular to it (left).



Figure 5. Dimensions of the pseudo-twist boat form of 1-phenylcyclohexane-1,4-diyl radical cation,  $10a^{+}_{\text{ptb}}$ .

local minimum; its relative enthalpy and its relative free energy at 298.14 K lie 12.0 and 13.8 kcal/mol, respectively, above those of **10a**<sup>•+</sup><sub>con</sub>. However, its unpaired electron spin density once again is localized either on C-1 (and the phenyl group) with the UMP2 method ( $\rho_1 = 0.79$ ,  $\rho_4 = 0.01$ ), or on C-4 with the UB3LYP method ( $\rho_1 = 0.11$ ,  $\rho_4 = 0.90$ , Table 2). The resulting hyperfine coupling patterns (Table 3) are incompatible with the experimental data.

A comparison between the hyperfine coupling patterns of **10a**<sup>++</sup><sub>ort</sub> and **10a**<sup>++</sup><sub>con</sub>, in particular the significant changes for H-4 and H-2,6<sub>ax</sub> with the UMP2 method ( $a_4$  changes from -29.92 to -7.63 G,  $a_{2,6ax}$  from 2.79 to 9.32 G) suggested that there might be a structure at an intermediate angle of twist, for which the hfcs would fit the experimental data. Accordingly, we examined additional species with twist angles between 0 and 90°; none of these structures are minima. The species with a twist angle of 60°, **10a**<sup>++</sup><sub>60°</sub>, has hfccs ( $a_4 = -18.92$  G, UMP2; = -16.11 G, UB3LYP;  $a_{2,6ax} = 10.73$  G, UMP2; = 8.00 G, UB3LYP) that show the closest agreement between  $|a_4|$  and  $|a_{2,6ax}|$  of any calculated form. Alas, even in this case the discrepancy is significant.

An alternative explanation for the ESR data involves a distortion of the electronic levels of  $10a^{++}$  by the strong

electrostatic fields inside zeolite voids.<sup>18</sup> These forces have been invoked to explain the remarkable stability of otherwise elusive positively charged intermediates in zeolites and they can affect the ordering of close-lying electronic states. For example, the ESR spectra of *cis*- and *trans*-decalin (bicyclo[4.4.0]decane) radical cations, cis-, trans-15<sup>•+</sup>, support the stabilization of two different "electronic states" (structure types), depending on the nature of the zeolite host and the temperature.<sup>19</sup> Spectra corresponding to the  ${}^{2}A_{1}$  state of *cis*-15<sup>•+</sup> were obtained in silicalite (a = 49.5 G, 4 H, 45K) or ZSM-34 (a = 50 G, 4 H), whereas spectra supporting the <sup>2</sup>A<sub>2</sub> state, predicted to be higher in energy by (vacuum) calculations, were observed in silicalite (a = 28.1 G, 4 H, 95 K) or offretite (a = 30.2 G, 4 H). For *trans*-15<sup>•+</sup>, structures corresponding to the (lower-energy)  $^{2}Ag$ state were observed in silicalite ( $a_{4H} = 50.5$  G) or ZSM 34 (a= 51.5 G, 4 H), whereas the higher-energy  $^{2}Bg$  state was supported in Na-Y (a = 28.5 G, 4 H) or Na-W-5 (a = 29.8G, 4 H).

Similarly, the ESR spectrum of *p*-methylphenoxyl radical, **16**•, in ZSM-5 showed a well-resolved 1:3:3:1 quartet ( $g = 2.0042 \pm 0.0001$ ; a = 14.6 G, 3 H; line width = 2.1 G),<sup>9b</sup> analogous to the known solution spectrum of **16**• ( $a_{\beta} = 11.95$  G, 3H;  $a_{2,6} = 6.0$  G, 2 H).<sup>20</sup> However, the species sequestered in the zeolite failed to reveal any evidence for coupling of the *o*-protons, which is significant in solution ( $a_{2,6} = 6.0$  G, 2 H).<sup>19</sup> In fact, the EPR spectrum of **16**•-aryl- $d_4$  showed a spectrum ( $a_{CH3} = 14.4$  G; line width = 1.3 G) very similar to that of **16**•-aryl- $h_4$  in the zeolite. These results were also ascribed to a distortion of the "conventional" phenoxyl radical, **16**•, by a specific interaction with the zeolite.

In light of these ESR results in zeolites we ascribe the results for  $10^{++}$  in ZSM-5 or H-mor, particularly the apparent limited delocalization of spin and charge into the phenyl group, to a distortion of the electronic structure of the sequestered guest by the strong electrostatic fields inside zeolite voids, an additional example of such a phenomenon. The unusual and unexpected results obtained in this study encourage further research into generating radical cations of unusual structure types in zeolites.

# Conclusion

Upon incorporation into a redox-active pentasil zeolite [(Na,H)-ZSM-5], 2-arylhexa-1,5-dienes (9; aryl = anisyl, tolyl, phenyl) are converted into 1-arylcyclohexane-1,4-diyl radical cations,  $10^{\bullet+}$ . The ESR spectrum of  $10^{\bullet+}$  (sextet, g = 2.0026; a = 9.0 G) indicated the presence of five essentially equivalent nuclei, indicating limited delocalization of spin and charge into the phenyl group. The limited delocalization is ascribed to the strong electrostatic fields inside zeolites. Species  $10^{\bullet+}$  is stable at room temperature, in striking contrast to the parent radical cation in cryogenic matrices: cyclohexane-1,4-diyl,  $3^{\bullet+}$  is converted to cyclohexene radical cation above 90 K. The structures of radical cation,  $10a^{\bullet+}$ , and of the unsubstituted parent were probed by density functional theory calculations.

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**Supporting Information Available:** Synthesis of donor molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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Incorporation of 2-Arylhexa-1,5-diene into Pentasil Zeolite

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