

Benzyne and related systems: an *ab initio* molecular orbital approach

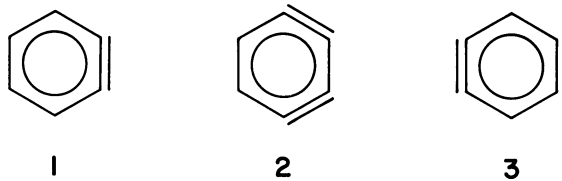
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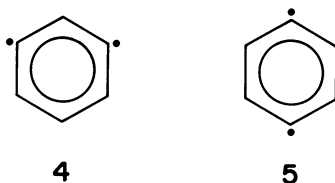
Abstract - *Ab initio* molecular orbital theory is used to study didehydro- and tetrahydro-aromatic systems. The molecules examined include the dehydro derivatives of benzene, furan, thiophene, pyrrole, pyrazole, imidazole, pyridine, pyridazine, pyrimidine and pyrazine. Optimized structures have been determined both for the parent aromatic systems and for the dehydro derivatives. Vibrational frequencies have been calculated for benzene, benzyne and their perdeutero derivatives. Complete-active-space self-consistent-field (CASSCF) and unrestricted Hartree-Fock (UHF) calculations have been used to provide an indication of the adequacy of a closed-shell single-configuration treatment for the arynes and heteroarynes.

INTRODUCTION

Didehydroaromatic systems, which can be generated formally by removal of a pair of vicinal hydrogen atoms from the parent aromatic molecule, form a class of reactive intermediates for which the prototype is 1,2-didehydrobenzene or benzyne (1). There is an extensive experimental literature both for benzyne itself and for its heterocyclic analogues, the didehydroheteroarenes or heteroarynes, as summarized in several comprehensive reviews (ref. 1-5). The dehydroaromatic molecules are highly reactive and, apart from infrared spectra of benzyne and tetra-deuterobenzyne, the experimental information on these systems is indirect. Indeed, recent critical reviews (ref. 4,5) have questioned whether didehydroheteroarenes are actually involved in many of the reactions for which their intermediacy has been postulated. Tetrahydroaromatic systems, formally generated by removal of two pairs of vicinal hydrogen atoms from the parent aromatic molecule and for which the prototypes are the pair of tetrahydrobenzenes or benzdiynes (2, 3), appear not to have been invoked to date as reaction intermediates.



There have been a number of theoretical papers dealing with benzyne, most of which are concerned with a comparison of 1,2-didehydrobenzene (1) with its 1,3- (4) and 1,4- (5) isomers (ref. 6-20).



The dehydroheteroarenes, on the other hand, have received relatively little theoretical attention and this has been restricted to date to semiempirical calculations (ref. 7, 21-24). No *ab initio* calculations have been reported for any of the didehydroheteroarenes nor for any of the tetrahydroaromatic systems.

In the light of the apparent experimental difficulties associated with the study of arynes and heteroarynes and the dearth of higher-level calculations performed on these systems,

we decided that a systematic *ab initio* study would prove useful. We have embarked on such a study and a selection of the results obtained to date is presented here. We have restricted our attention to *ortho* (as opposed to *meta* and *para*) dehydroaromatic systems i.e. those corresponding formally to removal of one or two pairs of *vicinal* hydrogens from the parent aromatic molecule. Such systems contain a triple bond in at least one of the contributing valence structures. It seems inappropriate to refer to *meta* or *para* dehydroaromatic systems as arynes or heteroarynes since their structures do not involve a (partial) triple bond; they have consequently not been included in the present study.

We stress that very little is currently known concerning the levels of theory required to describe adequately the dehydroaromatic systems. Consequently, the present study has a large exploratory component; some results, such as energy comparisons, are of a preliminary nature and should be treated with caution. A more comprehensive account, including more reliable energy comparisons, will be published in due course.

METHOD

Standard *ab initio* molecular orbital calculations were carried out using modified versions (ref. 25,26) of the Gaussian 80 (ref. 27) and Gaussian 82 (ref. 28) systems of programs. Geometry optimizations were performed, subject to symmetry constraints, using the spin-restricted Hartree-Fock (RHF) procedure with the 3-21G^(*) (ref. 29) and, in some cases, the 6-31G^{*} (ref. 30) basis sets. Although the symmetry choices appear reasonable in most instances, there is always the possibility that some of the species may distort or even ring open if the constraints were removed. Calculation of vibrational frequencies would be required to establish rigorously whether or not the structures we have obtained are indeed local minima on the appropriate potential energy surfaces. We have completed such frequency calculations for benzene and benzyne; calculations for several of the other species are in progress. The harmonic frequencies (3-21G//3-21G) were evaluated using a locally implemented version (ref. 31) of a symmetry-coordinate approach (ref. 32).

We have tested the validity of using a single closed-shell electron configuration to describe the dehydroaromatic systems by performing two additional sets of calculations. First, the constraint that the wavefunction be spin-restricted was relaxed, leading to an unrestricted Hartree-Fock (UHF) treatment (ref. 33). These UHF calculations were performed with the 6-31G (ref. 34) basis set. Second, multi-configurational self-consistent-field (MCSCF) calculations were carried out within the spin-restricted framework by using the complete-active-space SCF (CASSCF) method (ref. 35,36). These CASSCF calculations were performed with the 3-21G^(*) basis set using a modified version (ref. 37) of the GAMESS system of programs (ref. 38).

BENZENE AND PARENT HETEROCYCLES

Before discussing the dehydroaromatic systems, it is instructive to examine the performance of the theory for the parent aromatic molecules.

A comparison of our theoretical optimized structures with available experimental structural data (ref. 39) is presented in Figure 1. The description of the geometries of these systems provided by both the 3-21G^(*) and 6-31G^{*} basis sets appears quite reasonable. There are no very poor results: the largest errors in calculated bond lengths are 0.037 (3-21G^(*)) and 0.043 (6-31G^{*}) Å. The main deficiency in the calculated structures is a systematic tendency to overestimate the degree of bond alternation; use of larger basis sets and inclusion of electron correlation would be required to rectify this problem in an absolute sense (ref. 40). However, the *ordering* of the extent of bond alternation in different systems (e.g. furan > thiophene > pyrrole) is reproduced at the levels of theory used here.

A comparison of theoretical (3-21G//3-21G) and experimental (ref. 41) frequency data for benzene and hexadeuterobenzene is provided in Table 1. These data will be helpful in analysing the frequencies calculated for benzyne and its tetradeutero derivative. The results of Table 1 are consistent with previous comparisons (e.g. ref. 42) of 3-21G and experimental frequency data. After scaling by 0.9, the calculated values are generally within 5% of the experimental frequencies. A similar comparison has been published previously for MNDO calculated frequencies (ref. 18).

A final comparison with experiment for some reference systems is provided by the energy data in Table 2. The first two examples correspond to hydrogenation reactions while the last corresponds to ring opening of benzene. The errors at the 3-21G and 6-31G levels for these reactions are about 20-30 kJ mol⁻¹. For reactions involving dehydroaromatic molecules, however, the errors at these levels are likely to be significantly larger since an RHF treatment may often be inadequate (see below). Use of a UHF procedure is likely to be more satisfactory.

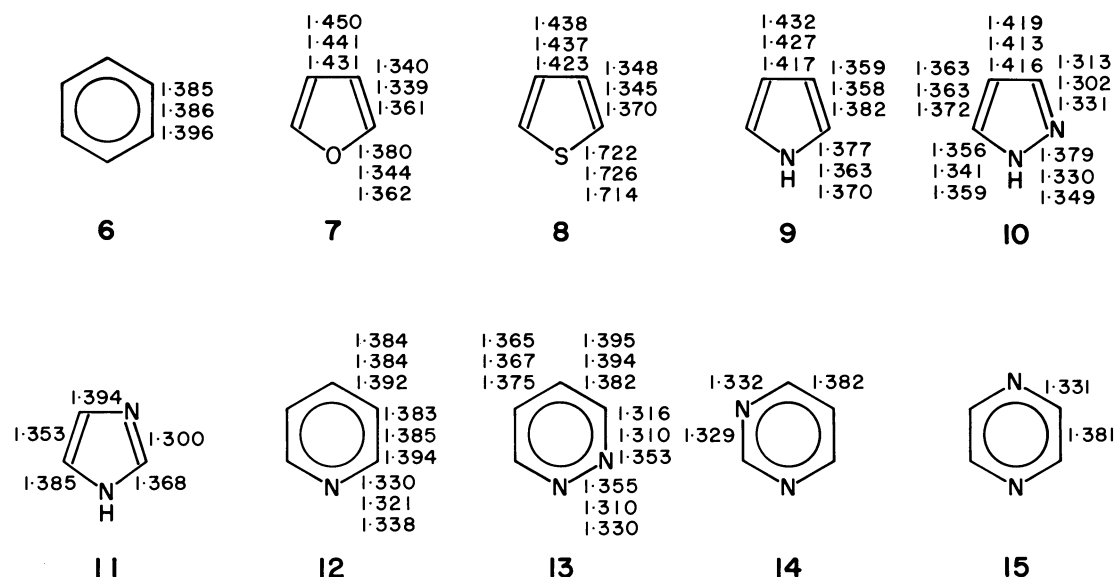


Fig. 1. Comparison of theoretical and experimental structural data for parent aromatic systems. Entries are in the order 3-21G^(*) followed, where available, by the 6-31G^{*} and experimental values.

Table 1. Comparison of calculated (3-21G//3-21G) and experimental vibrational frequencies (cm⁻¹) for benzene and hexadeuterobenzene

Approximate Mode	Symmetry	C ₆ H ₆			C ₆ D ₆		
		Calc. ^a	Calc. ^b	Exptl. ^c	Calc. ^a	Calc. ^b	Exptl. ^c
CH(D) stretch	a _{1g}	3388	3049	3062	2515	2264	2293
CH(D) stretch	e _{1u}	3374	3037	3063	2498	2248	2287
CH(D) stretch	e _{2g}	3355	3020	3047	2478	2230	2265
CH(D) stretch	b _{1u}	3345	3011	3068	2468	2221	2292
ring stretch	e _{2g}	1764	1588	1596	1706	1535	1552
ring stretch	e _{1u}	1658	1492	1486	1466	1319	1335
CH(D) bend	a _{2g}	1544	1390	1326	1201	1081	1037
CC stretch	b _{2u}	1366	1229	1310	1273	1146	1286
CH(D) bend	e _{2g}	1323	1191	1178	972	875	867
CH(D) bend	b _{2u}	1235	1112	1150	937	843	824
CH(D) bend	b _{2g}	1200	1080	995	1027	924	827
CH(D) bend	e _{2u}	1157	1041	975	947	852	795
ring deform.	b _{1u}	1148	1033	1010	1101	991	969
CH(D) bend	e _{1u}	1137	1023	1038	902	812	814
ring stretch	a _{1g}	1078	970	992	1028	925	943
CH(D) bend	e _{1g}	996	896	849	774	697	662
ring deform.	b _{2g}	820	738	703	678	610	601
CH(D) bend	a _{2u}	785	707	673	576	518	497
ring stretch	e _{2g}	698	628	606	666	599	577
ring deform.	e _{2u}	466	419	410	403	363	352

^a 3-21G//3-21G values.

^b Scaled by 0.9.

^c From ref. 41.

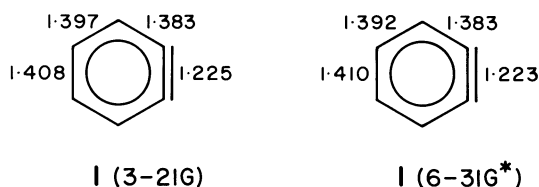
Table 2. Comparison of calculated and experimental reaction energies (kJ mol⁻¹)

Reaction	3-21G	6-31G	Exptl. ^a
HC≡CH + H ₂ → CH ₂ =CH ₂	-215	-223	-201
CH ₃ C≡CH + H ₂ → CH ₃ CH=CH ₂	-199	-205	-192
C ₆ H ₆ → 3HC≡CH	608	647	634

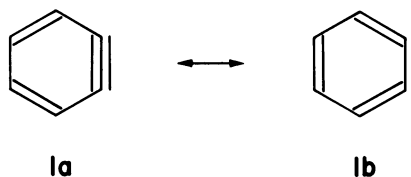
^a Calculated using data tabulated in W.J. Hehre, R. Ditchfield, L. Radom and J.A. Pople, *J. Am. Chem. Soc.* **92**, 4796 (1970); values listed have been corrected to 0 K and for zero-point vibrational energy.

DIDEHYDROBENZENE (BENZYNE)

We restrict our attention here to the *ortho* isomer of didehydrobenzene, or benzyne (1). Geometry optimizations were carried out initially at the RHF level with the 3-21G and 6-31G* basis sets. The results with the two basis sets are very similar and are consistent with those previously obtained at simpler levels of theory (ref. 14-20).



In particular, the calculated lengths increase along the sequence C₂-C₃ < C₃-C₄ < C₄-C₅, suggesting that any preference for valence structure **1a** compared with **1b**,



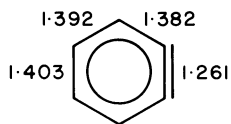
which may be expected on the basis of perturbation molecular orbital theory (ref. 24), is outweighed by geometric factors.

The calculated C₁-C₂ length is considerably shorter than the lengths of the other C-C bonds in benzyne and is only 0.04Å greater than the C≡C triple bond in acetylene, reflecting extensive overlap of the in-plane sp²-type orbitals at C₁ and C₂. However, the fact that the bond angles at C₁ and C₂ are far from 180° means that there may be significant biradical character associated with these atoms.

In order to examine the importance of biradical contributions, we have carried out two-configuration SCF (TCSCF) calculations using a CASSCF gradient program. The two configurations correspond to double occupation of one or other of the molecular orbitals which are predominantly the symmetric (S) and antisymmetric (A) combinations of the in-plane sp²-type orbitals at C₁ and C₂. In the limit of benzyne being a pure biradical, one would expect such a TCSCF treatment to lead to a substantial lengthening of the C₁-C₂ bond with the S² and A² configurations having almost equal weight in the final wavefunction.



In fact, the resulting optimized structure shows an elongation of C_1-C_2 of only 0.036 Å relative to the single-configuration value. The S^2 and A^2 configurations contribute 89% and 11% respectively to the total wavefunction.



I (TCSCF/3-21G)

For comparison, analogous TCSCF calculations were also carried out on *cis*-bent acetylene for various values of the CCH angles (maintaining C_{2v} symmetry). The results are consistent with those noted above for benzyne: decreasing the CCH angle from 180 to 120° (i.e. close to the value appropriate to benzyne) leads to an increase in the weight of the A^2 configuration from 3 to 12%. At 120°, the TCSCF treatment leads to a lengthening of the C≡C bond by 0.027 Å (cf 0.036 Å in benzyne).

An alternative means of exploring biradical character within the single-configuration framework is to allow the alpha and beta electrons to occupy different spatial orbitals. Such a relaxation of the constraint that the Hartree-Fock wavefunction be spin-restricted leads to a spin-unrestricted (UHF) treatment. For a species with significant biradical character, the RHF solution will be unstable, the UHF treatment leading to a lowering of the total energy. For example, 3-21G calculations on acetylene indicate that the RHF solution becomes unstable for HCC angles less than about 165°. On the basis of these calculations for acetylene, one would expect benzyne to be RHF unstable. Indeed, with the 3-21G basis, the UHF treatment leads to a lowering of the energy with respect to RHF by 87 kJ mol⁻¹. The UHF and TCSCF methods therefore both indicate that a single-configuration RHF description of benzyne is not entirely adequate.

No experimental structure for free benzyne has been reported to date. However, crystal structures of a tantalum complex $Ta(\eta^2-C_5Me_5)Me_2(\eta^2-C_6H_4)$ (ref. 43,44) and, more recently, of a quasi-square-planar nickel complex $Ni(\eta^2-C_6H_4)[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$ (ref. 45) have been obtained. The latter shows a C_1-C_2 bond, elongated through complex formation, of 1.332 Å, with the remaining C-C bonds in the aromatic ring lying in the range 1.385±0.005 Å.

The main experimental characterization of benzyne has come through the observation of the infrared spectra of the normal and tetradeuterated species in matrix-isolation experiments (ref. 46-48). We have calculated the harmonic vibrational frequencies of both species for comparison with the experimental results, as shown in Table 3.

The experimental data are incomplete, only 9 C_6H_4 frequencies and 11 C_6D_4 frequencies having been reliably established. Given that there are 24 normal modes, all of which will be nondegenerate under C_{2v} symmetry, the problems entailed in matching calculated and experimental frequencies become evident.

We have, nevertheless, attempted an assignment in Table 3, using the experimental frequencies reported by Dunkin and MacDonald (ref. 48). The only major difference between these frequencies and those of Chapman and co-workers (ref. 46) is the absence of a band at about 1627 cm⁻¹. For the theoretical frequencies, we adopted the approach shown to be successful for benzene (Table 1) in scaling the directly calculated 3-21G values by 0.9.

When this is done, several of the assignments in Table 3 are clear-cut and show good agreement between theory and experiment. This category includes the vibrations observed at 3088, 847, 743 and 472 cm⁻¹ in C_6H_4 and at 2293, 1108, 792, 730, 616 and 471 cm⁻¹ in C_6D_4 . There is a second category in which the assignment appears clear-cut but the agreement with experiment is less satisfactory. Examples here include the C≡C stretch at 2084 cm⁻¹ (2093 cm⁻¹ in C_6D_4), for which there is an error of about 100 cm⁻¹, and the b₂ CH bending vibration at 1598 cm⁻¹ (1483 cm⁻¹ in C_6D_4). Finally, for the remaining vibrations (1448, 1056 and 1039 cm⁻¹ in C_6H_4 and 1293, 1029 and 822 cm⁻¹ in C_6D_4), alternative assignments are possible but we feel that we have chosen that which is most probable on the basis of the information which is currently available. Further work is in progress with the aim of resolving the remaining uncertainties. In particular, the effect of carrying out the frequency calculations at the UHF/3-21G level rather than at RHF/3-21G is being explored.

Table 3. Comparison of calculated (3-21G//3-21G) and experimental vibrational frequencies (cm^{-1}) for benzyne and tetradeuterobenzyne

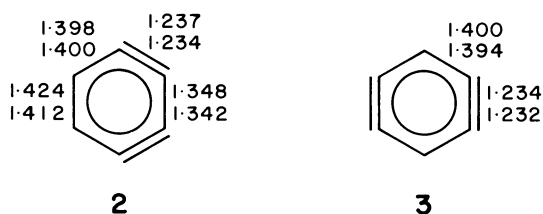
Approximate Mode	Symmetry	C_6H_4			C_6D_4		
		Calc. ^a	Calc. ^b	Exptl. ^c	Calc. ^a	Calc. ^b	Exptl. ^c
CH(D) stretch	a_1	3414	3072)		2532	2279)	
CH(D) stretch	b_2	3410	3069)	3088	2524	2272)	2293
CH(D) stretch	a_1	3375	3038)		2494	2245)	
CH(D) stretch	b_2	3357	3021)		2478	2230)	
$\text{C}\equiv\text{C}$ stretch	a_1	2209	1988	2084	2202	1981	2093
CH(D) bend	b_2	1614	1453	1598	1531	1378	1483
CH(D) bend	a_1	1604	1444	1448	1460	1314	1293
CH(D) bend	b_2	1542	1388		1395	1256	
CH(D) bend	a_1	1388	1250		1238	1114	1108
CH(D) bend	b_2	1363	1227		1097	987	
CH(D) bend	a_1	1259	1133	1056	1060	954	1029
CH(D) bend	b_2	1205	1085		954	859	
CH(D) bend	a_2	1158	1042	1039	973	876	822
CH(D) bend	b_1	1099	989		901	811	
ring stretch	a_1	1082	974		939	846	
CH(D) bend	a_1	1059	953		867	780	
CH(D) bend	a_2	1003	903		780	702	730
ring bend	b_2	956	861	847	890	801	792
CH(D) bend	b_1	859	773	743	662	596	616
ring bend	a_1	710	639		687	618	
ring bend	a_2	708	638		632	569	
ring bend	a_2	533	480		497	448	
ring bend	b_2	522	470	472	518	466	471
ring bend	b_1	449	404		385	347	

^a 3-21G//3-21G values.^b Scaled by 0.9.^c From ref. 48.

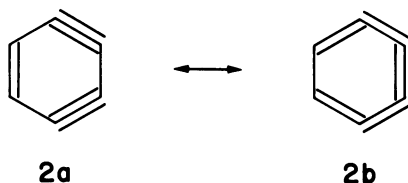
An experimental estimate of the heat of formation of benzyne has been obtained through an ion cyclotron resonance experiment (ref. 49). Combining this with the well-established heats of formation of hydrogen and benzene leads to a hydrogenation energy for benzyne of -411 kJ mol^{-1} . Our theoretical values are -498 (RHF/6-31G^{*}) and -416 (UHF/6-31G) kJ mol^{-1} . This comparison and results that we have obtained at the RHF level for various of the dehydroheteroarenes (e.g. relative energies for 1,2-, 3,4- and 2,3-didehydropyrrole of 0, 91 and 100 kJ mol^{-1} at RHF/3-21G compared with 0, -40 and -7 at CASSCF/3-21G and 0, -79 and -57 at UHF/6-31G) indicate that the RHF procedure may not be reliable for energy comparisons involving dehydroaromatic systems. Consequently, we restrict our discussion in the remainder of this paper to relative energies calculated at the UHF and CASSCF levels.

TETRADEHYDROBENZENES (BENZIDIYNES)

We are unaware of any theoretical or experimental work reported to date on the tetrahydrobenzenes or benzdiynes other than a brief examination using extended Hückel theory carried out as a preliminary to a study of dihydro-pyridines and -diazines (ref. 22). Removal of two pairs of vicinal hydrogens from benzene can lead formally to two different benzdiynes, namely 1,3-benzdiyne (2) and 1,4-benzdiyne (3). We have optimized the structures of both isomers and the results (in the order 3-21G followed by 6-31G*) are shown below.



The lengths of the partial triple bonds in 2 and 3 are quite close to those calculated for 1. The C_2-C_3 bond in 2 is noticeably short, analogous to the shortening of the central bond in 1,3-butadiene. The long C_5-C_6 bond shows again that any preference for valence structure 2a compared with 2b is outweighed by geometric factors which, through widening of the bond angles at C_1 , C_2 , C_3 and C_4 , lead to a lengthened C_5-C_6 bond.



CASSCF calculations were carried out on 2 and 3 in order to assess how well a single-configuration treatment describes these structures. In each case, the active space comprised four molecular orbitals: for 2, these were the highest occupied and lowest unoccupied orbitals of a_1 and b_2 symmetry, while for 3 the highest occupied a_g and b_{2u} orbitals and the lowest unoccupied b_{1u} and b_{3g} orbitals were chosen. This amounted to a twelve-configuration SCF for 2 and an eight-configuration SCF for 3. These calculations showed that, for both 2 and 3, the SCF configuration contributes only 79% to the total wavefunction.

At the CASSCF/3-21G level, 2 is found to lie lower in energy than 3 by 5 kJ mol^{-1} . However, at the UHF/6-31G level the ordering is reversed, 3 now being lower by 16 kJ mol^{-1} . It is clear that higher-level calculations are necessary to establish with any confidence which isomer is preferred.

Although neither of the free benzdiynes have yet been observed, a nickel complex $Ni_2(\eta^2-C_6H_2)[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]_2$, which corresponds in a formal sense to a bis(square-planar) nickel complex of 1,4-benzdiyne, has very recently been synthesized by Bennett and co-workers (ref. 50). It should be emphasized that the preparation of this complex did not actually involve benzdiyne as a reactive intermediate. The crystal structure shows that the distance between the carbons bound to nickel is 1.31 \AA whereas the remaining aromatic C-C bond lengths are in the range $1.41 \pm 0.01 \text{ \AA}$.

In a sense, since benzyne has been observed, albeit in a low-temperature matrix, it represents the benchmark against which to compare other dehydroaromatic systems. For example, calculated hydrogenation energies for the other dehydroaromatic molecules can be compared with that of benzyne. Table 4 lists such energies for benzyne, 1,3-benzdiyne and 1,4-benzdiyne. All of these reactions are predicted to be highly exothermic as expected. Surprisingly, however, it costs only about 80 kJ mol^{-1} more to remove two hydrogen atoms from benzyne than from benzene.

Table 4. Calculated energies (UHF/6-31G, kJ mol⁻¹) of formal reactions involving benzyne and the benzdiynes

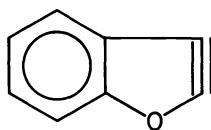
Reaction	ΔE
benzyne + H ₂ → benzene	-416
1,3-benzdiyne + H ₂ → benzyne	-506
1,4-benzdiyne + H ₂ → benzyne	-490
benzyne → HC≡CH + HC≡C-C≡CH	258
1,3-benzdiyne → HC≡C-C≡C-C≡CH	-223
1,4-benzdiyne → HC≡C-C≡C-C≡CH	-208

Table 4 also shows the energies of some formal reactions which compare the dehydrobenzenes with stable acyclic products. We have already seen in Table 2 that production of acetylene from benzene is highly endothermic. We now see in Table 4 that benzyne is also relatively stable when compared with acetylene plus butadiyne. However, the production of hexatriyne from either of the benzdiynes is predicted to be strongly exothermic.

Having noted the highly exothermic nature of the ring-opening of, for example, 1,3-benzdiyne, it is appropriate to reiterate that the geometry optimizations in this study were carried out subject to symmetry constraints, e.g. C_{2v} for 1,3-benzdiyne. Vibrational frequency calculations are in progress to establish whether such constraints are justified or whether there is a lowering of energy accompanying a lowering in symmetry.

DIDEHYDROHETEROARENES (HETEROARYNES)

The first dehydroaromatic molecule for which a structural formula appeared in the literature, some eighty years ago, was in fact a dehydroheteroarene, 2,3-didehydrobenzofuran (16) (ref. 51), rather than benzyne itself (1). A relatively

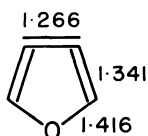


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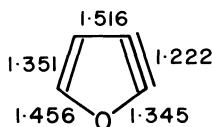
quiet period followed until the 1960s, at which stage dehydroheteroarenes were invoked as reaction intermediates for large numbers of reactions and 'heteroarynititis' was said to have been rife (ref. 5). More recently, the evidence for dehydroheteroarene involvement has been re-examined and results have been re-interpreted in many instances in terms of alternative mechanisms. Two excellent critical reviews on this subject have appeared within the last few years (ref. 4,5) and it is not intended, therefore, to dwell on this point here. It is sufficient to note that, although direct observation of a didehydroheteroarene has yet to be reported, there is strong indirect evidence for the existence, as reaction intermediates, of at least some of these species.

Didehydrofurans

There have been no previously reported theoretical or experimental studies of the didehydrofurans. Optimized 3-21G structures for the two possible isomers, 3,4-didehydrofuran (17) and 2,3-didehydrofuran (18), are shown below.



17



18

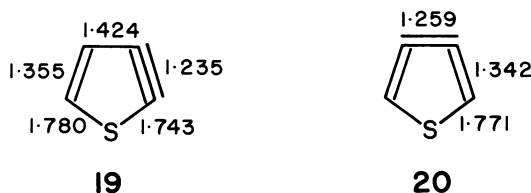
The former is favored at the UHF/6-31G level by 76 kJ mol⁻¹. Compared with furan, **17** shows a shortened C₃-C₄ bond (1.266Å) and an elongated C₂-O bond (1.416Å), as expected. The 2,3-didehydro isomer (**18**) is characterized by strikingly long C₃-C₄ (1.516Å) and O-C₅ (1.456Å) bonds and shortened O-C₂ (1.345Å) and C₂-C₃ (1.222Å) bonds. The angle at C₂ (128°) is also larger than expected. Many of these structural features can be explained in terms of the geometric requirements of π overlap of the in-plane partial-triple-bond orbitals, as discussed previously for benzyne and the benzdiynes, and the interaction of the oxygen in-plane lone pair with the partial triple bond. The bond alternation in **18** is the strongest of the five-membered didehydroheteroarenes, as is the case with furan compared with the other parent heterocycles.

CASSCF calculations were performed for **17** and **18**, using initially for **17** the highest occupied a₁ and lowest unoccupied b₂ orbitals and for **18** the highest occupied and lowest unoccupied a' orbitals as the active space. By analogy with benzyne, we can label these orbitals "S" and "A", corresponding approximately to the symmetric and antisymmetric combinations of the aryne in-plane sp²-type orbitals. Note that, because of the reduced symmetry, this leads to a three- rather than a two-configuration SCF for **18** (and indeed for some of the other didehydroheteroarenes discussed below), the configurations being "S²", "SA" and "A²". However, in all cases, the "SA" configuration has a negligible weight in the final wavefunction. The weights of the "S²" configurations in **17** and **18** are each 83%, somewhat smaller than the 89% found for benzyne. This is probably indicative of the poorer overlap possible in the five-membered ring compared with the six-membered ring of benzyne. With the 3-21G basis set, this two-orbital CASSCF treatment gives a preference for **17** compared with **18** of 62 kJ mol⁻¹.

Additional CASSCF calculations were carried out with the aim of examining the effect of expanding the active space to three orbitals by including the orbital which corresponds roughly to the in-plane lone pair on oxygen. The effect of this change was found to be very small. The contribution of the "S²" configuration remained at 83% in both **17** and **18** and the energy difference between **17** and **18** changed by only 1 kJ mol⁻¹ (to 63 kJ mol⁻¹).

Didehydrothiophenes

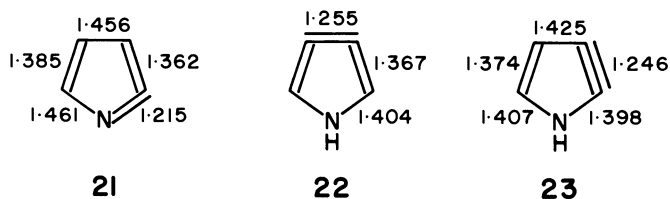
These species have been the most studied experimentally of the five-membered heteroarynes (ref. 3) and have also been examined previously at an elementary theoretical level (ref. 7). We find, at the CASSCF/3-21G level, that 2,3-didehydrothiophene (**20**) lies just 1 kJ mol⁻¹ lower than the 3,4-isomer (**19**). With three orbitals in the active space, the contributions of the "S²" configuration are 90% and 85% for **19** and **20**, respectively.



The structural similarities between **17** and **20** are quite clear. However, **18** and **19** show marked differences. For example, the C₃-C₄ bond, noted to be very long (1.516Å) in **18**, is shorter in 2,3-didehydrothiophene (**19**) than in thiophene (**8**). Again, the widening of the angle at C₂ in **18** (128° compared with 110° in furan) is replaced by a narrowing of that angle in **19** (102° compared with 112° in thiophene). Finally, shortening of the O-C₂ bond in **18**, indicative of conjugative interaction of the oxygen lone pair with the partial triple bond, does not carry over to a shortening of the S-C₂ bond in **19**.

Didehydropyrroles

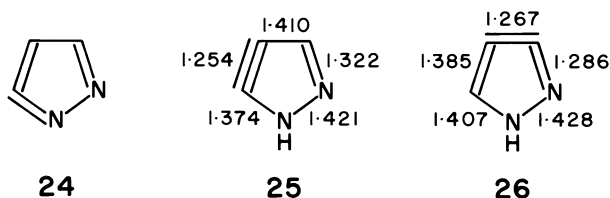
There have been no previous theoretical studies of these systems and experimental evidence for their existence is inconclusive (ref. 4). We have examined three isomeric didehydropyrroles. At the UHF/6-31G level, the 3,4-didehydro isomer (**22**) lies lowest in energy with 2,3-didehydropyrrole (**23**) and 1,2-didehydropyrrole (**21**) lying 22 and 79 kJ mol⁻¹, respectively, higher in energy. Corresponding relative energies at the CASSCF/3-21G level are 0, 33 and 40 kJ mol⁻¹ for **22**, **23** and **21**.



The contribution of the "S²" configuration in the CASSCF treatment is much greater for 21 than for 22 and 23 (97% compared with 84% and 82%) and this variation in the adequacy of the single-configuration description leads to the poor RHF estimates of relative energies noted earlier. The dominance of the single configuration for 21 may be attributed to the different electronegativities and hence different orbital energies of the atoms making up the partial triple bond. Such a disparity in orbital energies decreases the extent of biradical character (ref. 52). We also note that 21 is one of only three didehydroaromatics for which the RHF solution is found to be stable with respect to maintaining the equivalence of the alpha and beta spin orbitals.

Didehydropyrazoles

Calculations on 1,5-didehydropyrazole (24) with an idealized geometry lead to an RHF/3-21G energy lower than that of optimized structures of the 4,5- (25) and 3,4- (26) isomers.

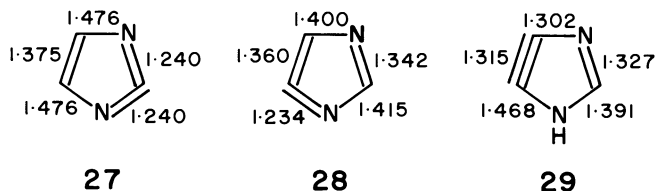


However, 24 is found to ring open without a barrier through rupture of the N-N bond. The remaining two isomers are stable, with 25 lying lower than 26 by 26 (UHF/6-31G) or 12 (three-orbital CASSCF) kJ mol⁻¹.

The structure of 4,5-didehydropyrazole (25) is quite unremarkable in the light of the discussion of the previous dehydroaromatic systems. On the other hand, the 3,4-didehydro isomer (26) shows structural features which confirm those hinted at in 2,3-didehydrofuran (18): the presence of a nitrogen atom adjacent to the partial triple bond enables its lone pair to participate in conjugation with the in-plane π system. The result is a severely bent isoelectronic analogue of the allyl anion. Comparison of 26 with the structures obtained for 22, 25 and pyrazole itself (10) shows a shortening in 26 of N₂-C₃, a lengthening of C₃-C₄ and a widening (to 129°) of the bond angle at C₃, all reflecting this allyl-anion-type interaction.

Didehydroimidazoles

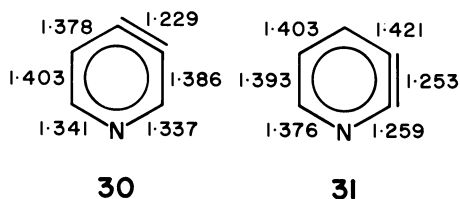
The lowest-energy isomers of didehydroimidazole are those which incorporate a nitrogen in the partial triple bond. There are two such isomers (27, 28), with 1,2-didehydroimidazole (27) being the preferred form. At the UHF/6-31G level, the 1,5-isomer (28) lies 36 kJ mol⁻¹ higher in energy and the 4,5-isomer (29) lies 119 kJ mol⁻¹ above 27. The corresponding CASSCF relative energies are 0, 32 and 121 kJ mol⁻¹. Because of symmetry, 27 represents an extreme of the allyl-anion-type delocalization. The two nitrogen atoms are equivalent, the N₁-C₂ and C₂-N₃ bonds are equal and significantly shortened, and the angle at C₂ is widened to 137°.



The CASSCF calculations indicate that, for 27, 28 and 29, the SCF configurations strongly dominate the wavefunction, the respective weights being 99, 97 and 99%. Consistent with this result, the RHF/6-31G solutions for 27 and 29 are stable.

Didehydropyridines

The didehydropyridines have been examined in several semiempirical molecular orbital studies (ref. 7, 21-23). With the exception of simple Hückel calculations (ref. 21), the remaining theoretical predictions indicate 3,4-didehydropyridine (30) to be more stable than 2,3-didehydropyridine (31) (ref. 7,22,23). The 3,4-isomer was, in fact, the first heteroaryne to be proposed in modern times (ref. 53) and the evidence for its existence is the strongest of that for any heteroaryne (ref. 4).



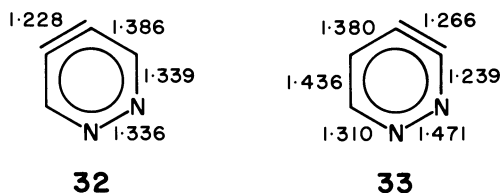
Our UHF/6-31G calculations favor **30** over **31** by 56 kJ mol⁻¹, while at the CASSCF/3-21G level the energy difference is very similar: 58 kJ mol⁻¹ (two active orbitals) or 57 kJ mol⁻¹ (three active orbitals). The contributions of the "S²" configuration for **30** and **31** are, respectively, 91 and 92% at both the two-active-orbital and three-active-orbital levels. It is encouraging to see that inclusion of an additional orbital (corresponding roughly to the in-plane lone pair at nitrogen) in the active space has only a marginal effect.

Experimental results for the dehydrohalogenation of 3-halogenopyridines (ref. 54) suggest the intermediacy of 3,4-didehydropyridine (**30**) rather than 2,3-didehydropyridine (**31**). This does not necessarily reflect the relative stabilities of **30** and **31** but may be due to the greater stability of the 4-pyridinyl anion (the precursor of **30**) compared with the 2-pyridinyl anion (the precursor of **31**) (ref. 22,55).

The calculated structure of **31** indicates substantial allyl-like delocalization of the nitrogen lone pair into the partial triple bond. Again, this is reflected in a slight lengthening of the partial triple bond, a shortening of the adjacent C-N bond, and a widening of the bond angle at C₂ (to 146°) in **31** compared with **30**.

Didehydropyridazines

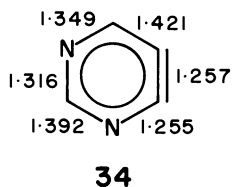
Previous EHT (ref. 22) and MNDO (ref. 24) calculations have predicted that 4,5-didehydropyridazine (**32**) lies lower in energy than the 3,4-isomer (**33**). Our calculations agree, with a predicted energy difference of 147 (UHF/6-31G) or 50 (CASSCF/3-21G) kJ mol⁻¹.



Potentially, 3,4-didehydropyridazine (**33**) could show in-plane conjugation formally analogous to that of a severely bent butadiene dianion. However, it is clear from the calculated structure that the in-plane π system in **33** resembles a four-electron allyl-like unit, analogous to that of 2,3-didehydropyridine (**31**), and a nitrogen lone pair which does not participate significantly in the conjugation. For example, the bond lengths within the NCC unit are remarkably similar to corresponding lengths in **31** and the angle at C₂ is widened to about 146°. The weakness of the interaction of the lone pair at N₁ with the NCC unit is also reflected in a long N₁-N₂ bond (1.471 Å) and a small angle (about 105°) at N₂.

Didehydropyrimidines

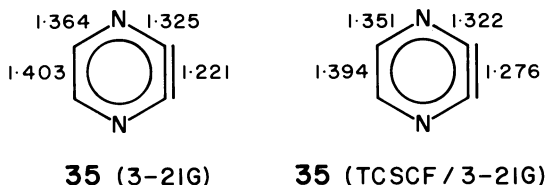
Only a single ortho isomer of the didehydropyrimidines, namely the 4,5-isomer (**34**), can be drawn and its optimized structure is shown below.



Again, the heteroallylic four-electron delocalization can be seen, with bond lengths and angles similar to those of other six-membered heteroarynes. The C₅-C₆ bond is noticeably long (1.421 Å).

Didehydropyrazines

Again, only one *ortho* isomer can be drawn for the didehydropyrazines, namely the 2,3-isomer (35). Previous MNDO calculations (ref. 24) have indicated a large degree of biradical character for this molecule and some unusual geometric features (e.g. a C₂-C₃ length of 1.66Å) which are changed markedly at the MNDO/CI level. In order to examine this effect, we have optimized the structure of 35 at both the single-configuration and two-configuration levels.

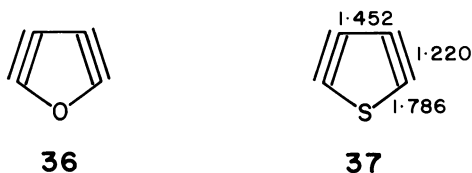


We find a small decrease in the contribution of the S² configuration in 35 compared with benzyne (82% compared with 89%) but the structural changes are modest. We have subsequently carried out MNDO calculations and find, in addition to the structure with C₂-C₃ = 1.6Å, a lower-energy minimum which resembles the 3-21G structures obtained here.

TETRADEHYDROHETEROARENES

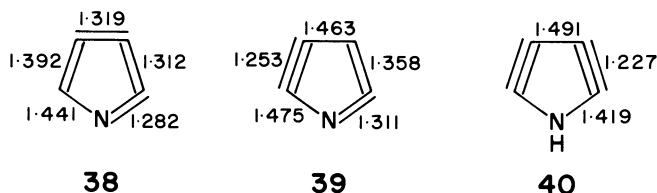
We are unaware of any previous theoretical or experimental studies of any of the tetrahydroheteroarenes. A selection of our results is discussed briefly below.

Our calculations on tetrahydrofuran (36) showed spontaneous rupture of the C₃-C₄ bond. On the other hand, tetrahydrothiophene (37) possesses a perfectly respectable structure.



This difference in behaviour is consistent with the differences noted in the C₃-C₄ lengths in 2,3-dihydrofuran (18, 1.516Å) and 2,3-dihydrothiophene (19, 1.424Å).

Pyrrole possesses three stable tetrahydro derivatives, 38-40.



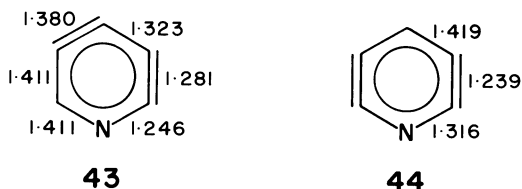
Both CASSCF/3-21G and UHF/6-31G calculations predict that 2,3,4,5-tetrahydropyrrole (40) is the preferred isomer. At the former level, 39 and 38 lie, respectively, 31 and 41 kJ mol⁻¹ higher in energy; corresponding relative energies at UHF/6-31G are considerably higher at 139 (39) and 138 (38) kJ mol⁻¹.

Tetrahydropyrazole (41) and tetrahydroimidazole (42) are both unstable.



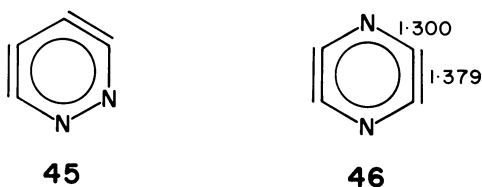
The former undergoes rupture of the N-N bond, which is not surprising given that even the didehydropyrazole (24) is similarly unstable. The tetrahydroimidazole (42) ring opens to give (under a C_{2v} symmetry constraint) di-isocyanomethylene (CNCNC).

There are two stable tetrahydropyridine isomers, **43** and **44**.



2,3,5,6-Tetrahydropyridine (**44**) is slightly favored (by 8 kJ mol⁻¹ at CASSCF/3-21G). Structure **43** is characterized by strikingly long C₄-C₅ (1.380Å) and short C₃-C₄ (1.323Å) bonds.

Tetrahydropyridazine (**45**) spontaneously ring opens by means of rupture of the N-N bond, noted already to be weak in 3,4-didehydropyridazine (**33**). On the other hand, tetrahydropyrazine (**46**) is found to be stable, at least under a D_{2h} symmetry constraint. The length of the C-C partial triple bond in **41** (1.379Å) is noticeably longer than that in **35** (1.221Å).



CONCLUDING REMARKS

Apart from benzyne itself, experimental information for the other dehydroaromatic systems is virtually all indirect and consequently often inconclusive. Theory has the opportunity to play a useful role in characterizing such molecules. We would hope that information of the type presented in the present article might prove useful in experimental studies of the dehydroaromatic molecules. Our study has revealed some of the deficiencies of a closed-shell single-configuration treatment in energy comparisons involving dehydroaromatic molecules. Further work is in progress with the aim of obtaining more reliable results through the use of UHF, unrestricted Møller-Plesset (UMP) and CASSCF procedures, and larger basis sets.

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