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META- AND PARA-PHENYLENEDINITRENE: AN AB INITIO COMPUTATIONAL STUDY

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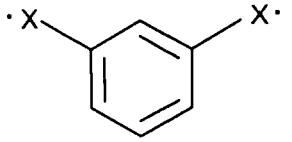
Abstract Geometry optimizations and MRSDCI calculations were performed on the isomeric compounds m- and p-phenylenedinitrene (**1 a** and **2**) employing basis sets of up to DZP in quality. The ground state of **1 a** was predicted to be a quintet in agreement with experiment. The quinoid form of **2** is predicted to be the ground state structure in agreement with recent experiments and has near degenerate triplet and singlet states.

INTRODUCTION

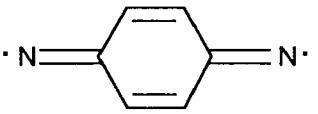
In the m-phenylene coupled series of radicals **1** (Scheme 1), qualitative theories[1,2] have predicted that the ground state of each species will be high-spin. Experimental studies found that m-phenylenedinitrene **1 a**, and m-benzoquinodimethane **1 b**, are a ground state quintet and triplet respectively, while m-quinone **1 c**, has not yet been observed.[3,4] Ab initio computations on **1 b**[5] and **1 c**[6] predict the triplet-singlet (TS) gap to be approximately 10 and 8 kcal/mol respectively. The replacement of methylene groups by oxygen did not greatly perturb the magnitude of the TS splitting, although the lowest singlet state of m-quinone was found to be an open-shell state in contrast to the lowest singlet state of **1 b**.[6] The preference for the high-spin ground state does not change with nitrene substitution. However, a nitrene substituent has two unpaired electrons so that m-phenylenedinitrene is somewhat different electronically from the isoelectronic species **1 b** and **1 c**. It is therefore interesting to compute the relative energies of the lowest lying states of **1 a** to compare the effect nitrene substituents on the magnitude of the energy separation between high and low-spin states.

Previous ESR experiments on **2** (Scheme 1), have observed a triplet spectrum which differed significantly from that of phenylnitrene indicating that the carrier of the ESR signal possessed a different structure.[7,8] However,

Scheme 1



X
N · 1a
CH_2 1b
O 1c



2

none of the published studies have presented conclusive data suggesting that the triplet is the ground state. Interestingly, the D-value obtained from the ESR spectrum of **2** ($|D|=0.174\ cm^{-1}$)[8] was very large for two separated, localized electrons that are not conjugated. Therefore, in order to predict the ground state and hopefully to shed some light on the above observation, the second part of this study involved computing the geometries and relative energies of the lowest lying states of **2**.

COMPUTATIONAL METHODOLOGY

The geometries of the various electronic states of open-shell pi-conjugated radicals are best computed by multi-configuration (eg. MCSCF) wavefunctions.[10] Ideally, the geometry of each electronic state of **1 a** would be optimized using MCSCF methodology, since a minimal description of the triplet and singlet states requires that the four unpaired electrons be distributed among four orbitals. Unfortunately, such calculations employing basis sets of split-valence plus polarization quality were beyond our computational means. However, under favorable circumstances, the geometry of the state with the highest spin multiplicity optimized with a UHF wavefunction may closely approximate one obtained with more sophisticated MCSCF wavefunctions.[10]

Therefore, the geometry of the quintet state of **1 a** was optimized in C_{2v} symmetry with both UHF and ROHF wavefunctions employing the D95v* (Dunning-Hay [9s5p/3s2p] plus 'd' functions on carbon and nitrogen; $\alpha_d(C)=0.75$ and $\alpha_d(N)=0.80$) basis set,[11] and these geometries were used in all subsequent multi-reference singles and doubles CI calculations (MRCISD) of each spin multiplicity. The lowest triplet and singlet states of **2** possessing D_{2h} symmetry were optimized with UHF and GVB wavefunctions respectively employing both the 6-31G* ($\alpha_d(C)=\alpha_d(N)=0.8$)[12] and D95v* basis sets. The quintet state of **2** was optimized with both UHF and ROHF wavefunctions for comparison. In addition, further refinements of the triplet and singlet geometries of **2** were obtained by individually optimizing the N=C and C=C bonds with limited SDCI wavefunctions using the 6-31G* basis set.

Geometry optimizations were carried out with the Gaussian90[13] package of ab initio programs with the exception of the SDCI optimized geometries which used the MELDF suite of ab initio programs.[14]

MRSDCI calculations were carried out for **1 a** and **2** using MELDF employing both the 6-31G* basis for geometries optimized with this basis, and the Dunning double zeta plus polarization[15] (DZP) basis sets for all D95v* geometries. A slightly better basis set on hydrogen was used in the DZP calculations.[16] The MRSDCI used 6, 16, and 17 for the quintet, triplet, and singlet states respectively. These configurations were chosen from MCSCF/-STO-3G calculations and included all configurations with coefficients greater than 0.05. Because an enourmous number of spin adapted configurations (SACs) was generated by MELD, second order perturbation theory and a reduced active space were used to truncate the MRSDCI. The energetic threshold for keeping a configuration was 5×10^{-7} hartrees. The number of SACs and the orbital active space used in the MRSDCI calculations of **1 a** are also given in Table I.

All singles and doubles CI (SDCI) calculations reported for **2** used 1 and 2 reference configurations for the triplet and singlet states respectively. A limited active space was used to truncate the SDCI instead of second order perturbation theory, because the energy differences were very small and the latter method gave inconsistent results. The number of SACs and the orbital active space used in the SDCI calculations of **2** are given in Table II.[17]

RESULTS and DISCUSSION

The optimized UHF and ROHF geometries of the quintet state of **1 a** are given in Figure 1. As expected,[10] the UHF geometry is more delocalized than the ROHF geometry. However, since the UHF wavefunction was contaminated by states of higher multiplicity, <S2>=6.74, the delocalization may be somewhat overestimated by this method. A recent ab initio study on phenyl-

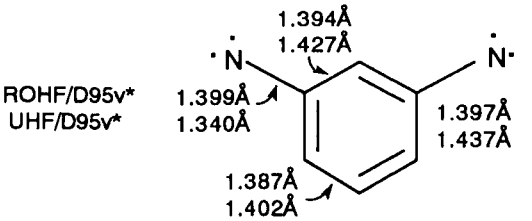


Figure 1. Comparison of selected geometric parameters of **1 a**.

nitrene by Kim et al. found the triplet geometry computed at the DZ+d/SDCI level of theory to have bonding para-meters similar to aniline suggesting that delocalization of the unpaired spin does not result in significant distortion of the phenyl ring for this molecule.[18] The largest difference was in the N-C bond length, 1.402Å, which actually shortened to 1.388Å upon inclusion of CI.[18] This result suggests that the relatively localized quintet ROHF geometry may be a somewhat better approximation of the bonding in **1 a**, even though the N-C bonds are probably too long at 1.399Å.

This contrasts somewhat with a recent ab initio study of **1 c** which found that delocalization of the unpaired electron spin in the triplet state resulted in short O-C bonds, 1.231Å, and long C-C bonds, 1.433-1.456Å at the π-SDCI/6-31G* level of theory.[6] Hence, partial formation of a N=C double bond may not be as energetically favorable for **1 a** as it is for **1 c**. Further refinement of the molecular geometries using MCSCF or MRCI correlated wavefunctions employ-ing at least the D95v* or 6-31G* basis set would be essential for resolving this question. It is worth noting that at the MRSDCI/DZP level of theory, the UHF-D95v* geometry is lower in energy by 0.34 kcal/mol (Table I). However, this difference is small, and since the spin contamination of the UHF wavefunction was fairly large, it is likely that the best description of the bonding in this molecule is intermediate between the UHF and ROHF geometries.

The quintet state is found to be the ground state of m-phenylenedinitrene in agreement with experiment. The ΔE's are somewhat dependent on the

Table I MRSDCI energies of the $^5A_1$, $^3B_2$, and $^1A_1$ states of **1 a**.

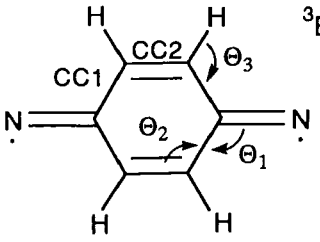
Geometry[a]	State	Energy(a.u.)	ΔE[b]	#SACs[c]
$^5A_1$ UHF	$^5A_1$	-338.509972	0.0	28,161
(20,24)[d]	$^3B_2$	-338.500685	5.8	38,808
	$^1A_1$	-338.492844	10.7	19,639
$^5A_1$ ROHF	$^5A_1$	-338.509391	0.0	25,313
(20,24)[d]	$^3B_2$	-338.503412	3.7	36,582
	$^1A_1$	-338.499488	6.2	19,130
$^5A_1$ ROHF	$^5A_1$	-338.626169	0.0	91,353
(28,33)[d]	$^3B_2$	-338.620533	3.5	133,173
	$^1A_1$	-338.617322	5.5	70,925

[a] Optimized with the D95v* basis set. [b] In kcal/mol relative to the quintet state. [c] The number of spin adapted configurations kept after second order perturbation selection of configurations. [d] The orbital active space consisted of X electrons in Y orbitals (X, Y).

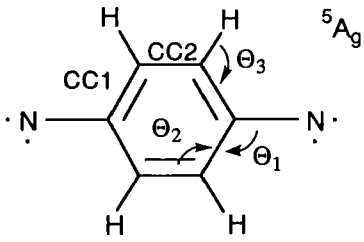
geometry and active space. The UHF geometry provides larger vertical energy differences than the ROHF geometry, while a slightly larger active space tends to decrease the energy gaps. As previously mentioned, the quintet energy is lower at the UHF geometry by a small amount. However, the $^3B_2$ and $^1A_1$ states are significantly lower at the $^5A_1$ ROHF geometry by 1.7 and 4.2 kcal/mol respectively. Although the MRSDCI used a rather limited active space considering the size of the molecule and the number of basis functions, it is unlikely that further refinements of the molecular geometry or increasing the size of the CI would result in a reversal of the state ordering as indicated in Table 1.

Selected optimized geometries of **2** are compared in Table II and the relative SCF and SDCI energies are given in Table III. The triplet and singlet 6-31g* geometries computed with UHF and GVB wavefunctions were very similar and differed significantly only in the N=C bond lengths (UHF/6-31G* r_{NC}= 1.264Å). When the N=C and C=C double bonds were individually optimized for both states at the SDCI level, the N=C bond lengths were virtually identical so only the triplet SDCI/6-31G* geometry is shown. The ^5A_g ROHF geometry differed significantly from the UHF geometry only in a slightly longer N-C bond length (r_{NC}=1.410Å). Unfortunately, it was not possible to compute the singlet D95v*/GVB geometry with our resources so adiabatic energy differences were not computed with the DZP basis set. However, the SDCI energy of the ^1A_g state was always lower at the triplet geometry for all other calculations employing the 6-31G* basis set. Therefore, only the SDCI energies computed at the triplet geometries are shown in Table III.[17]

TABLE II Optimized p-phenylenedintrene parameters. Bond lengths are reported in angstroms and bond angles in degrees.



$^3B_{1u}$ ^1A_g



^5A_g

Geometry	N-C	CC1	CC2	C-H	Θ1	Θ2	Θ3
$^3B_{1u}$ UHF/D95v*	1.270	1.485	1.328	1.075	121.0	121.0	117.4
$^3B_{1u}$ CISD/6-31g*	1.265	1.482	1.330	1.074	121.1	121.1	117.2
^1A_g GVB/6-31g*	1.251	1.479	1.324	1.074	121.1	121.1	117.2
^5A_g UHF/D95v*	1.406	1.396	1.389	1.076	119.9	119.9	119.7

The lowest SDCI energies and energy differences were obtained at the triplet D95v*/UHF geometry employing the DZP basis set correlating all 38 valence electrons in a total of 49 orbitals. The triplet is predicted to be the ground state by only 60 cal/mol at this level of theory, with or without the inclusion of the Davidson correction[19] for quadruple excitations. This contrasts with the prediction of a singlet ground state by qualitative models based on valence bond theory.[2] An atomic spin population analysis at the SDCI/6-31G* level showed that the unpaired electron spins were largely localized in almost pure nitrogen 'p' type (n_{2py}=0.90; n_{total}=0.95) atomic orbitals. There is very little computed unpaired spin on the carbon atoms or in the sigma bonding framework. Hence, it is not entirely clear why the D-value is so large for this molecule.

In a recent experimental study by Minato et al.,[7] the connectivity related biphenyl-4,4'-dinitrene **3** (Scheme 2), was determined to be a GS singlet based on the decrease in intensity of the ΔM_S=2 peak with temperature of the

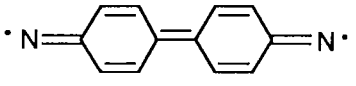
Table III Relative SCF and SDCI energies of **2** computed at different geometries.

Geometry	State	Method	Energy(a.u.)	ΔE^c	#SACs[d]
$^3B_{1u}$	$^3B_{1u}$	ROHF	-338.38701	0.0	
UHF/D95v*	"	SDCI	-338.88020	0.0	86,583
(38, 49)[b]	"	SDQCI[a]	-338.95741	0.0	
	^1A_g	TCSCF	-338.38696	0.06	42,699
	"	SDQCI[a]	-338.95732	0.06	
^5A_g	^5A_g	ROHF	-338.37747	6.0	
UHF/D95v*					
$^3B_{1u}$	$^3B_{1u}$	ROHF	-338.32899	0.0	
SDCI/6-31g*	"	SDCI	-338.75942	0.0	78,304
(30,52)[b]	"	SDQCI[a]	-338.82221	0.0	
	^1A_g	TCSCF	-338.32894	0.03	
	"	SDCI	-338.75913	0.18	36,170
	"	SDQCI[a]	-338.82185	0.23	
^5A_g	^5A_g	ROHF	-338.31768	7.1	
UHF/6-31g*					

[a] Including the Davidson correction for quadruple excitations.[19] [b] The active space consisted of X electrons in Y orbitals, (X, Y). [c] All energy differences are in kcal/mol. ΔE_{SDCI}(S-T)=0.60 kcal/mol at the triplet UHF/6-31G* geometry. The adiabatic ΔE_{SDCI} between the singlet GVB/6-31G* and triplet UHF/6-31G* geometries is 1.0 kcal/mol. [d] The number of spin adapted configurations.

triplet ESR spectrum. Additionally, a ground state singlet was found for the hydrocarbon analogue p-phenylenedicarbene **4**.[7,20] Although this evidence sug-gests that our ab initio result may be qualitatively wrong, our prediction of very nearly degenerate states is reasonable if the ESR signal observed for **2** resulted from a thermally accessible triplet state lying only slightly above the singlet GS. Nevertheless, the TS gap predicted at the current level of theory is small enough that further refinements of the geometries with better basis sets and a larger CI could conceivably change the predicted state ordering.

Scheme 2



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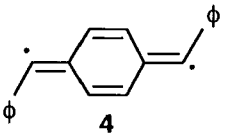

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It was not possible to compute the SDCI energy of the ^5A_g state with the identical active spaces used for the triplet and singlet states due to limitations in our computational resources. However, a recent matrix isolation IR study of **2** supports the qualitative prediction at the SCF level that the quintet state lies significantly above the quinoid structures of the triplet and singlet states.[21] The experimentally observed bands at 1759 cm^{-1} and 1775 cm^{-1} were assigned to the N=C stretching of the quinoid structure.[21] A vibrational analysis showed the $^3B_{1u}$ D95v*/UHF geometry to be a stationary point on the potential energy surface. The computed frequency of 2021 cm^{-1} corresponds reasonably well with the observed frequencies when scaled by a typical SCF correction factor of 0.90[22] (1819 cm^{-1}), and can be assigned to the asymmetric N=C stretch based on a normal coordinate analysis.

SUMMARY

m-Phenylenedinitrene was predicted to be a ground state quintet in agreement with experiment. MRSDCI calculations at different quintet geometries suggest that the energy differences between the quintet, triplet, and singlet states are in the range ΔE_{QT}=3.5-5.8 kcal/mol and ΔE_{TS}=2.0-4.9 kcal/mol. The lowest energy structure of p-phenylenedinitrene was found to be quinoidal with nearly degenerate singlet and triplet states with a small preference for the triplet by 60 cal/mol at the SDCI/DZP level of theory.

ACKNOWLEDGEMENTS

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