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The C_7H_5 Fulvenallenyl Radical as a Combustion Intermediate: Potential New Pathways to Two- and Three-Ring PAHs

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This study proposes the existence of a new, highly resonantly stabilized free radical, fulvenallenyl (C_7H_5). Fulvenallenyl forms from dissociation or abstraction of the weak H atoms in the C_7H_6 compounds fulvenallene and 1-ethynylcyclopentadiene, which were recently identified as intermediates in the combustion of aromatic fuels and in sooting flames. The fulvenallenyl radical shares properties of the propargyl and cyclopentadienyl radicals, and like these species, we propose that fulvenallenyl has a significant resonance stabilization energy. This resonance energy is lost upon further reaction, making the fulvenallenyl radical resistant to oxidation and thermal decomposition. As with the resonantly stabilized radicals propargyl and cyclopentadienyl, fulvenallenyl is expected to react with other radicals in molecular weight growth reactions. Several pathways are proposed for self-reaction and cross-reactions of fulvenallenyl that directly produce two- and three-ring PAHs like naphthalene, diphenyl, and phenanthrene. Rate constants are calculated for H atom abstraction from fulvenallene and 1-ethynylcyclopentadiene by the common radicals H, OH, and CH_3, to facilitate the inclusion of fulvenallenyl in kinetic models.

Introduction

It has been known for some time that C_7H_6 species form as intermediates during combustion.[1] Uncertainty regarding their structure has, however, precluded the inclusion of C_7H_6 chemistry in detailed combustion models. Recently, both experimental and theoretical studies have proposed fulvenallene and 1-ethynylcyclopentadiene as the major C_7H_6 combustion intermediates, finally opening up C_7H_6 chemistry for development.

The first identification of specific C_7H_6 isomers came in a photoionization mass spectrometry study of a cyclopentene flame by Hansen and co-workers.[2] Here, significant levels of C_7H_6 compounds were observed, presumably formed in the cyclopentadienyl (c-C_5H_5) + acetylene (C_2H_2) reaction,[2] an important process in the formation of polyaromatic hydrocarbons (PAHs). C_7H_6 was attributed to either fulvenallene or 1-ethynylcyclopentadiene, but similarities in their photoionization efficiency spectra prevented an unambiguous identification. Using a similar experimental technique, large quantities of a C_7H_6 species identified as fulvenallene[3] have been observed in the combustion[4] and pyrolysis[5] of toluene. In a rich toluene flame peak fulvenallene levels were around half of that of the benzyl radical,[4] the primary oxidation product of toluene. At around the same time, theoretical studies predicted that fulvenallene (+ H) would be the major decomposition product of the benzyl radical,[6] with barriers for formation significantly lower than those for other proposed products, like c-C_5H_5 + C_2H_2. Subsequent kinetic modeling of species profiles in a rich toluene flame supports fulvenallene as a decomposition product of benzyl.[7] Fulvenallene and substituted alkyl fulvenallenes are also predicted to form in the decomposition of alkyl benzyl radicals.[8] A recent theoretical study has shown how both fulvenallene and 1-ethynylcyclopentadiene can be formed in the c-C_5H_5 + C_2H_2 reaction[9] and can be interconverted via their reactions with free H atoms (favoring the more-stable fulvenallene).

It is apparent that the C_7H_6 compounds fulvenallene and/or 1-ethynylcyclopentadiene are important intermediates in oxidation and pyrolysis processes relevant to PAH formation and the combustion of aromatic hydrocarbons. In combustion systems, high-molecular-weight PAHs coagulate to form soot particles, which are a major human health concern[10] and contribute to anthropogenic global warming.[11] Aromatic hydrocarbons are one of the largest single components of liquid transportation fuels, and their production from biomass makes them potential green fuels.[12] Detailed kinetic models are currently used to optimize aromatic combustion and reduce soot formation in internal combustion engines, and the kinetics and thermochemistry of C_7H_6 species needs to be included in these models.

This study is concerned with the initial oxidation chemistry of fulvenallene and 1-ethynylcyclopentadiene. Computational chemistry is used to show that these C_7H_6 compounds possess low energy C−H bonds that cleave to form a C_7H_5 radical termed fulvenallenyl. We consider this species to be a highly resonance stabilized free radical, possessing characteristics of both propargyl (CH_2CCH) and c-C_5H_5. We demonstrate that in thermal systems, the fulvenallenyl radical will be removed slowly by oxidation and decomposition processes and is therefore expected to contribute to PAH formation via similar reactions to its analogues propargyl and c-C_5H_5. When compared to these other radicals, however, molecular weight growth

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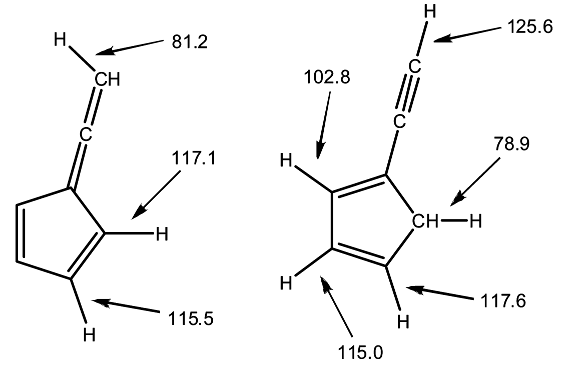


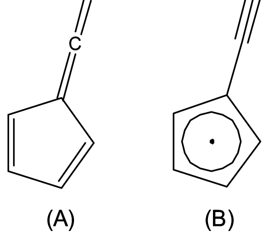
Figure 1. Bond dissociation energies (BDEs, kcal mol^{-1}) in the C_7H_6 compounds fulvenallene (left) and 1-ethynylcyclopentadiene (right).

reactions from fulvenallenyl lead to PAHs that are larger by one or two rings.

Results and Discussion

The major initial pathways for the destruction of fulvenallene and 1-ethynylcyclopentadiene in flames will be via bimolecular radical addition and abstraction reactions along with unimolecular decomposition. Molecule−molecule reactions like fulvenallene + C_2H_2 may also play a role[13] but are expected to require significant activation barriers. Bond dissociation energies (BDEs) for all C−H bonds in fulvenallene and 1-ethynylcyclopentadiene have been calculated at the G3SX level of theory and are illustrated in Figure 1. In both molecules, the most weekly bonded H atoms are at the CH_2 sites, where the BDEs are around 80 kcal mol^{-1}. Loss of H atoms from the ring CH sites, in comparison, requires large amounts of energy, as is known for similar five-membered ring compounds[14] (dissociation of the ≡C−H hydrogen in 1-ethynylcyclopentadiene forms a high-energy ethynyl-type radical; this is included for illustrative purposes only).

Loss of H atoms from the CH_2 sites in fulvenallene and 1-ethynylcyclopentadiene should dominate in the decomposition and abstraction reactions of these compounds. The C_7H_5 radical that forms from these C_7H_6 species is termed the fulvenallenyl radical, and it is calculated to have a standard heat of formation of 113.4 kcal mol^{-1} (thermochemical properties are provided in Table 1). This radical possesses resonance structures similar to the propargyl radical, where the allenic ($CH_2{=}C{=}C{\bullet}H$) and acetylenic ($C{\bullet}H_2{-}C{\equiv}CH$) forms are available. The CH_2CCH−H bond in allene, which leads to the propargyl radical + H, has a BDE of around 89 kcal mol^{-1},[15] and the much lower BDE of 81.2 kcal mol^{-1} for the analogous bond in fulvenallene suggests a significantly higher degree of stabilization in the fulvenallenyl radical. The added stability of fulvenallenyl likely arises from its ability to delocalize the radical electron into the C_5 ring, providing it with cyclopentadienyl-like resonance structures (B), in addition to the allenic structure (A), as depicted below.



The fulvenallenyl radical appears to possess resonance structures that are common to both the propargyl and cyclopentadienyl radicals. It should be noted that unlike the cyclopentadienyl radical, however, fulvenallenyl (which has C_{2v} symmetry) does not experience Jahn−Teller distortion. The weak C−H bond in cyclopentadiene has a BDE of 82.5 kcal mol^{-1},[16] whereas the corresponding BDE in 1-ethynylcyclopentadiene is only 78.9 kcal mol^{-1}. This implies some additional stabilization of fulvenallenyl over cyclopentadienyl, consistent with a contributing allenic resonance structure (the resonance stabilization energy of cyclopentadienyl is considerably greater than that of propargyl). Further work is required, however, to identify the relative contributions of the different resonance structures in fulvenallenyl and to determine its resonance stabilization energy.

Transition states have been located for H atom abstraction from fulvenallene and 1-ethynylcyclopentadiene by the typical radicals H, OH, and CH_3. Enthalpies of reaction ($\Delta_rH^\circ_{298}$) and activation ($\Delta^{\ddagger}H^\circ_{298}$) for abstraction of the weak H atoms in both C_7H_6 compounds are listed in Table 2. In all cases, the reactions are considerably exothermic, resulting in small activation barriers. In comparison, abstraction reactions at the higher-energy CH sites in fulvenallene and 1-ethynylcyclopentadiene require significantly larger barriers (at least 16.4, 2.3, and 16.5 kcal mol^{-1} for respective reaction with H, OH, and CH_3). This will result in small branching ratios to these other C_7H_5 radicals, particularly for H and CH_3 (OH is less selective). Additionally, because abstraction by OH requires essentially no barrier, this process, which should be favored in terms of entropy, will compete with or even dominate over OH addition.

Rate constants have been calculated for fulvenallenyl formation in the reactions of fulvenallene and 1-ethynylcyclopentadiene with H, OH, and CH_3, with fitted rate parameters A', n, and E_a listed in Table 3. For these abstraction reactions, pre-exponential factors ($A'T^n$) at 1000 K are around 5×10^{13} cm^3 mol^{-1} s^{-1} for abstraction by H, 6×10^{12} cm^3 mol^{-1} s^{-1} for abstraction by OH, and 2×10^{12} cm^3 mol^{-1} s^{-1} for abstraction by CH_3. For the fulvenallene + OH reaction, the G3SX method predicts a small negative activation barrier (−1.2 kcal mol^{-1}), typically characteristic of the formation of a prereactive complex. Intrinsic reaction coordinate scans, however, indicate that this transition state leads directly to dissociated fulvenallene + OH. The negative barrier appears to be an artifact of the composite theoretical methodology, where single-point energy calculations are performed using B3LYP-optimized structures. Accordingly, rate constants for this reaction have been estimated by setting the activation enthalpy to zero.

Resonance stabilization in the fulvenallenyl radical suggests that it may be a relatively long-lived combustion intermediate. The major processes for radical destruction in flames are thermal decomposition (typically homolytic bond scissions) and oxidation (typically by O_2). The propargyl and c-C_5H_5 radicals are resistant to both oxidation and decomposition, and this makes them long-lived and available to participate in bimolecular reactions that lead to cyclic hydrocarbons, establishing them as major PAH precursors.[17] Similarly, the fulvenallenyl radical is resistant to C−H β-scissions, with BDEs of 124.9 and 123.5 kcal mol^{-1} for loss of the respective 2- and 3-position ring H atoms. Other decomposition reactions are no doubt available, but no low-energy pathways are obvious. Addition of O_2 at the 1-, 2- and 3-position ring sites in fulvenallenyl is exothermic by only 2.0, 8.2, and 7.8 kcal mol^{-1}, respectively, while addition at the allenic CH site is exothermic by 9.0 kcal mol^{-1}. The small well depths for O_2 addition to the fulvenallenyl radical, due to the loss of resonance, provides these unstable $C_7H_5O_2$

TABLE 1: Thermochemical Properties ($\Delta_f H°_{298}$ in kcal mol^{-1}, $S°_{298}$ and $C_p(T)$ in cal mol^{-1} K^{-1}) for the Fulvenallenyl Radical

	$\Delta_f H°_{298}$	$S°_{298}$	C_p 300	C_p 400	C_p 500	C_p 600	C_p 800	C_p 1000	C_p 1500	C_p 2000
fulvenallenyl	113.4	78.69	25.74	32.64	38.06	42.26	48.29	52.46	58.73	61.95

TABLE 2: Enthalpies of Reaction ($\Delta_r H°_{298}$) and Activation ($\Delta^{‡} H°_{298}$) for Abstraction of H Atoms from CH_2 Sites in Fulvenallene and 1-Ethynylcyclopentadiene[a]

	$\Delta_r H°_{298}$	$\Delta^{‡} H°_{298}$
fulvenallene + H	−23.3	5.0
fulvenallene + OH	−38.3	−1.2
fulvenallene + CH_3	−23.8	6.7
1-ethynylcyclopentadiene + H	−25.5	4.5
1-ethynylcyclopentadiene + OH	−40.5	0.8
1-ethynylcyclopentadiene + CH_3	−26.1	5.9

[a] Values in kcal mol^{-1}. Calculated at the G3SX level of theory.

TABLE 3: Rate Constant Parameters for Abstraction of H Atoms from CH_2 Sites in Fulvenallene and 1-Ethynylcyclopentadiene[a]

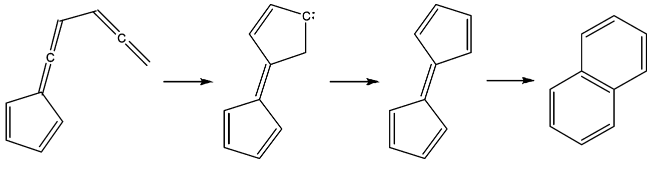
	A' (cm^3 mol^{-1} s^{-1})	n	E_a (kcal mol^{-1})
fulvenallene + H	1.90×10^8	1.847	4.965
fulvenallene + OH	1.20×10^5	2.621	−0.515
fulvenallene + CH_3	1.87×10^4	2.724	6.008
1-ethynylcyclopentadiene + H	1.08×10^8	1.812	4.491
1-ethynylcyclopentadiene + OH	3.50×10^4	2.688	0.293
1-ethynylcyclopentadiene + CH_3	6.90×10^3	2.730	5.246

[a] $k = A'T^n \exp(-E_a/RT)$ cm^3 mol^{-1} s^{-1}. Valid from 300 to 2000 K.

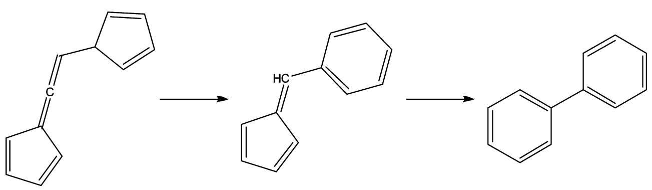
adducts with little excess vibrational energy for further activated reactions. The reverse dissociation of these adducts to fulvenallenyl + O_2 will be fast, with slow forward reactions to new products (this is also a characteristic of propargyl).[18] We suggest that fulvenallenyl oxidation will predominantly occur via reactions with species like O(^{3}P) and OH, which are typically present at much lower levels than O_2, particularly in sooting flames.

Due to the stability of the fulvenallenyl radical, we hypothesize that under molecular weight growth conditions it predominantly participates in bimolecular reactions with hydrocarbons and other resonance-stabilized radicals. In this study, we present a preliminary exploration of this chemistry, specifically the fulvenallenyl self-reaction and the fulvenallenyl + propargyl/c-C_5H_5 cross-reactions. Detailed experimental and theoretical kinetic studies will, however, be required to quantify the actual mechanisms and reaction rates. Furthermore, many other processes involving hydrocarbons like C_2H_2 and benzene, and radicals like allyl and vinyl, may also be important.

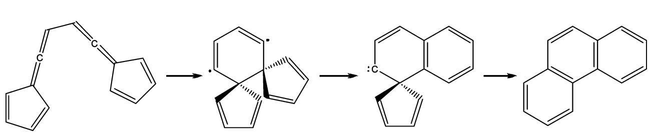
The highly complex propargyl self-reaction[19] is known as an important source of the cyclic compounds fulvene, benzene, and the phenyl radical (+ H) in sooting flames. Analogously, we expect the fulvenallenyl + propargyl reaction to yield naphthalene and other C_{10} polycyclic compounds. The fulvenallenyl + propargyl association produces a range of initial products that can isomerize to bicyclic compounds with five- and six-membered rings. One potential pathway, proceeding via fulvalene, is shown below (the final rearrangement of fulvalene to naphthalene actually requires several steps, but this process is well-known).[20] Current kinetic models assume that the benzyl + propargyl reaction and the c-C_5H_5 self-reaction are the major sources of naphthalene (+ 2H) in aromatic combustion, and we suggest that the fulvenallenyl + propargyl reaction may supplement these processes. The reaction of fulvenallene with propargyl may also contribute to naphthalene formation (+ H).



The fulvenallenyl + c-C_5H_5 reaction can also proceed via addition at the allenic and ring sites. The allenic addition process is illustrated below, where we envisage a hydrogen shift reaction taking place, with subsequent rearrangement to a $C_{12}H_{10}$ phenylfulvene compound. Following this, a benzene−fulvene rearrangement can yield diphenyl. The formation of diphenyl is significantly underpredicted by kinetic models for toluene combustion.[7]



The fulvenallenyl self-reaction should also produce a number of molecular weight growth products, in this case with formula $C_{14}H_{10}$. Below, we depict a potential pathway to phenanthrene from the product formed by addition at the two allenic sites. Three-membered PAHs like phenanthrene and acenaphthylene (a $C_{12}H_8$ compound that is another potential product of fulvenallenyl + c-C_5H_5, along with 2H) are detected in sooting aromatic flames. Typically, secondary reaction chemistry (like HACA) involving two-ring PAHs is used to explain their formation, but the present chemistry provides a direct formation route from the oxidation/decomposition products of toluene.



In conclusion, we have demonstrated that fulvenallenyl is an important free radical with a high degree of resonance stabilization. This radical is resistant to β-scission reactions and oxidation by O_2 and is expected to play a significant role in PAH growth reactions. While further work is required to quantify the PAH-forming potential of fulvenallenyl, it is clear that this radical will be present in combustion systems and that pathways should be directly available to many of the two- and three-ring PAHs observed in sooting aromatic flames.

Computational Methods

Calculations were performed using the Gaussian 03 program.[21] All reported energies are G3SX 298 K enthalpies.[22] Standard enthalpies of formation ($\Delta_f H°_{298}$) are from atomization calculations, with entropy and heat capacity values calculated from standard statistical mechanical principles. Abstraction rate constants are calculated according to canonical transition-state theory between 300 and 2000 K. Internal rotation about $C\cdots H\cdots CH_3$ in the CH_3 abstraction transition states is treated with a free rotor model, with RRHO treatment for all other modes.

Supporting Information Available: Cartesian coordinates, G3SX energies, and vibrational frequencies for fulvenallenyl. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) McAllister, T.; Scott, J. D. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 63. (b) Braun-Unkhoff, M.; Frank, P.; Just, T. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1417. (c) Fröchtenicht, R.; Hippler, H.; Troe, J.; Toennies, J. P. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 33.

(2) Hansen, N.; Kasper, T.; Klippenstein, S. J.; Westmoreland, P. R.; Law, M. E.; Taatjes, C. A.; Kohse-Höinghaus, K.; Wang, J.; Cool, T. A. *J. Phys. Chem. A* **2007**, *111*, 4081.

(3) Due to the similar PIE spectra, it is not clear if the observed C_7H_6 is actually fulvenallene or 1-ethynylcyclopentadiene.

(4) Li, Y.; Zhang, L.; Tian, Z.; Yuan, T.; Wang, J.; Yang, B.; Qi, F. *Energy Fuels* **2009**, *23*, 1473.

(5) Zhang, T.; Zhang, L.; Hong, X.; Zhang, K.; Qi, F.; Law, C. K.; Ye, T.; Zhao, P.; Chen, Y. *Combust. Flame* **2009**, *15*, 2071.

(6) (a) da Silva, G.; Cole, J. A.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 6111. (b) Cavallotti, C.; Derudi, M.; Rota, R. *Proc. Combust. Inst.* **2009**, *32*, 115.

(7) Detilleux, V.; Vandooren, J. *J. Phys. Chem. A* **2009**, doi: 10.1021/jp905954g.

(8) da Silva, G.; Moore, E. E.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 10264.

(9) da Silva, G.; Cole, J. A.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, submitted.

(10) Dockery, D. W.; Pope, C. A.; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G.; Speizer, F. E. *N. Engl. J. Med.* **1993**, *329*, 1753.

(11) (a) Ramanathan, V.; Carmichael, G. *Nat. Geosci.* **2008**, *1*, 221. (b) Shindell, D.; Faluvegi, G. *Nat. Geosci.* **2009**, *2*, 294.

(12) Carlson, T. R.; Tompsett, G. A.; Conner, W. C.; Huber, G. W. *Top. Catal.* **2009**, *52*, 241.

(13) da Silva, G.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 8971.

(14) (a) da Silva, G.; Moore, E. E.; Bozzelli, J. W. *J. Phys. Chem. A* **2006**, *110*, 13979. (b) Simmie, J. M.; Curran, H. J. *J. Phys. Chem. A* **2009**, *113*, 5128.

(15) Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766.

(16) Roy, K.; Braun-Unkhoff, M.; Frank, P.; Just, T. *Int. J. Chem. Kinet.* **2001**, *33*, 821.

(17) (a) Pope, C. J.; Miller, J. A. *Proc. Combust. Inst.* **2000**, *28*, 1519. (b) Richter, H.; Howard, J. B. *Prog. Energy Combust. Sci.* **2000**, *26*, 565.

(18) Hahn, D. K.; Klippenstein, S. J.; Miller, J. A. *Faraday Discuss.* **2001**, *119*, 79.

(19) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 7783.

(20) Melius, C. F.; Colvin, M. E.; Marinov, N. M.; Pitz, W. J.; Senkan, S. M. *Symp. (Int.) Combust.* **1996**, *26*, 685.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(22) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

JP907230B