THE STABILITY OF $C_6H_6^{+2}$: THE IMPLICATION FOR POLYCYCLIC AROMATIC HYDROCARBON DICATIONS

MARZIO ROSI

CNR ISTM, Department of Chemistry, University of Perugia, I-06100 Perugia, Italy

CHARLES W. BAUSCHLICHER, JR.

NASA Ames Research Center, Space Technology Division, MS 230-3, Moffett Field, CA 94035; charles.w.bauschlicher@nasa.gov

AND

E. L. O. BAKES

SETI, NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035

ABSTRACT

The fragmentation pathways of $C_6H_6^{+2}$ are studied using density functional theory. All of the transition states that were found, excluding the rearrangement to the C_{5v} structure, are significantly above the six-membered ring structure. This is consistent with the soft ionization experiments that find mostly dication production instead of fragmentation. Since the C_{5v} structure is probably of limited importance for multiple-ring polycyclic aromatic hydrocarbons, the computed barriers suggest that Coulomb explosion is not a significant channel under most astrophysical conditions, and therefore, the dications are long-lived and should be considered in modeling of the interstellar medium.

Subject headings: astrochemistry — ISM: molecules — molecular processes

*On-line material:* color figure

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been proposed (Allamandola et al. 1989; Szczepanski & Vala 1993; Puget & Léger 1989) as the carriers of the unidentified IR bands that have been observed in a number of astrophysical sources. On the basis of computer modeling and laboratory experiments, it has been concluded that for most conditions the PAHs are ionized (DeFrees et al. 1993; Joblin et al. 1994; Langhoff 1996; Cook & Saykally 1998; Piest et al. 1999; Hudgins et al. 2001; Bakes et al. 2001b). PAHs dominate the heating and cooling of the interstellar medium (ISM) via photoelectric ejection (Draine 1978; Bakes & Tielens 1994). The PAHs are highly efficient absorbers of ultraviolet (UV) radiation, which means they contribute considerably to interstellar UV opacity. In the PAHs the absorbed UV radiation is converted from electronic to vibrational energy, and, as a result, they show strong IR emission features between 3.3 and 12.7 μm and beyond.

The size of the PAH molecules in interstellar sources has been estimated at 50–200 carbon atoms (Allain et al. 1996a, 1996b; Hudgins & Allamandola 1999; Schutte et al. 1993). For PAH molecules in this size range, the second ionization energy is expected to be below the 13.6 eV cutoff in UV radiation; therefore, some of the PAH species could exist as dications. This idea has not received a lot of attention, largely because of a lack of experimental information about the dications.

In recent calculations (Bauschlicher & Bakes 2000), we found that the IR bands of the dications are as strong as, or stronger than, those of the cations. The positions of the dication bands are very similar to those of the cation, and therefore it would be difficult to detect the existence of dications based on observations alone. We have also modeled

(Bakes et al. 2001a) the IR emission from neutral and charged PAHs. This model showed that the charge state of the PAH species depends on the ratio of the Habing radiation field G_0 to the electron density n_e. As shown in Figure 5b of Bakes et al. (2001a), there are nontrivial dication populations for a G_0/n_e ratio greater than about 10^3 for species with more than 24 carbon atoms. For a ratio of 10^4, the dications can exceed the cations. We should note that the dications are assumed to be stable in this modeling study. Therefore, if they are stable, the PAH dications could be as important in understanding the ISM as the PAH neutrals or cations.

Leach (1987) considered formation and destruction mechanisms for PAH dications. For large PAHs, the second ionization energy is below 13.6 eV, and a sizeable population of cations is believed to exist; therefore, the most likely dication formation mechanism is by the ionization of PAH cations. Because the energy of a dication is above the energy of two cationic fragments, the dications are metastable. However, there is a barrier to this fragmentation process that can be quite large, leading to very long lived species. For example, $LaFe^{+2}$ was found (Huang & Freiser 1988) to have an exceptionally long lifetime, which we computed (Bauschlicher & Langhoff 1989) to be 10^{600} s. As noted by Leach (1987), even if the tunneling lifetime is very long, the dication can absorb radiation that leads to dissociation, either by an electronic transition to a dissociative excited state or vibration excitation to a level near the barrier (or a metastable state above the barrier). Leach also pointed out that if the geometry of the cation and dication are very different, the dication could be formed with sufficient excess energy so that tunneling would occur very rapidly, if not immediately (i.e., Coulomb explosion). Unfortunately, little is known about the lifetimes of PAH dications. Early experiments formed dications with large quantities of excess energy, and Coulomb explosion was observed (see,

Fig. 1.—Heats of reactions in kcal mol^{-1}.
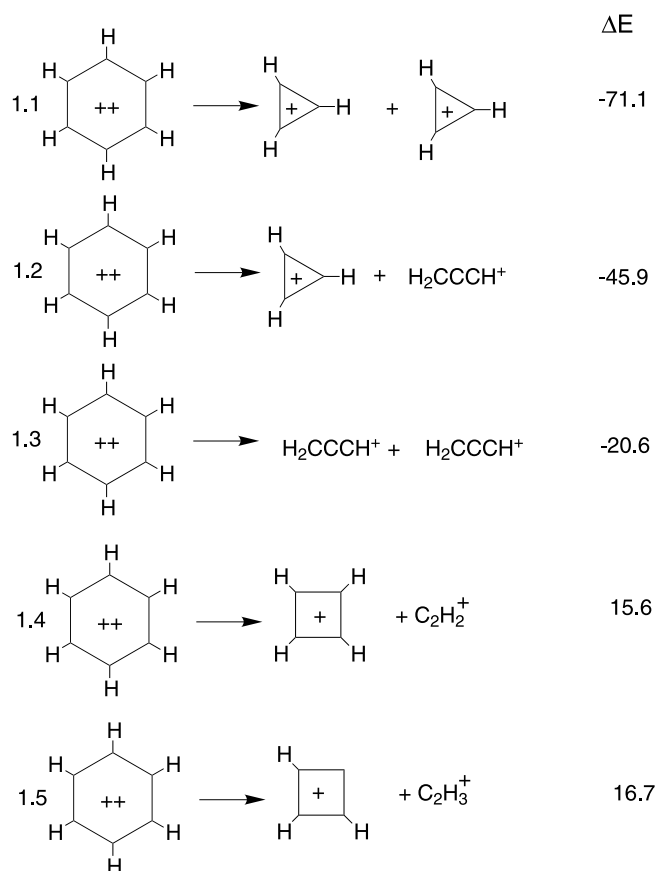
Fig. 2.—Barriers and heats of reactions in kcal mol^{-1}.

e.g., Leach et al. 1989), but more recent experiments (Ledingham et al. 1999) have used soft ionization and observed mostly dication production. Soft ionization experiments are expected to produce conditions similar to those in the ISM. Unfortunately, the lifetimes of the dications have not been determined in these soft ionization experiments.

In light of the dication production in soft ionization experiments, our calculations that show that dications have strong IR bands, and our modeling that shows significant dication populations under some conditions, it seems timely to investigate the stability of the dications. Ideally, we should study the stability of a PAH dication containing between 50 and 200 carbon atoms, the current estimate for the size of PAHs in interstellar sources. Unfortunately, for species this large, it would be very difficult to study all of the possible dissociation paths in a reasonable amount of time. While benzene is not of significant interest from an interstellar modeling point of view, it is the simplest aromatic molecule and can be used to investigate possible PAH dication dissociation paths. Some paths, such as the breaking of a C-H bond, are expected to be very similar for benzene and the larger PAHs, while others, such as the breaking of C-C bonds, are expected to be easier for benzene than larger PAHs, since benzene does not have any additional rings to resist C-C bond breaking. Thus, benzene can be used to obtain some idea of the stability of more relevant PAHs, and in this manuscript we report on the barrier heights for possible dissociation paths for the benzene dication. The size of the barrier should help determine if the dications have sufficiently long lifetimes to be included in models of the ISM.
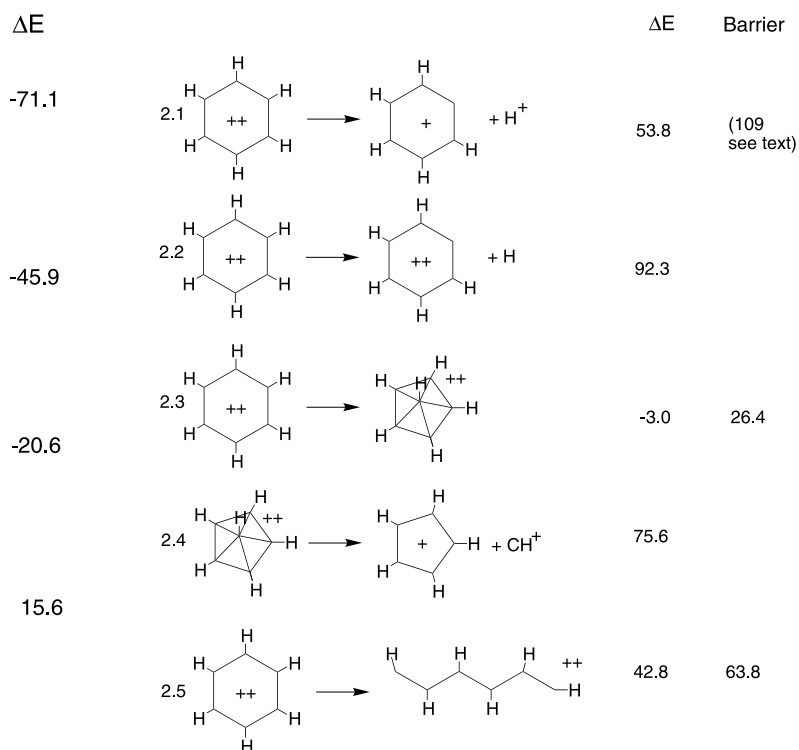
2. MODEL AND METHODS

The geometries were optimized and the harmonic frequencies were computed using the B3LYP (Stephens et al. 1994) hybrid (Becke 1993) functional in conjunction with the 6-31G* basis sets (Frisch et al. 1984 and references therein). The frequencies confirmed that we have either minima or transition states. We computed the zero-point energy as one-half the sum of the B3LYP harmonic frequencies. The calculations were performed using the Gaussian 98 computer code (Frisch et al. 1998).

One set of calibration calculations is performed using the coupled-cluster singles and doubles approach, including the effect of connected triples determined using perturbation theory [CCSD(T); Raghavachari et al. 1989], in a correlation-consistent polarized valence triple zeta basis set (cc-pVTZ; Kendall et al. 1992). The CCSD(T) calculations are performed using the MOLPRO code (Werner & Knowles 2002).

3. RESULTS AND DISCUSSION

We first consider the difference between the vertical and adiabatic second ionization energy at the B3LYP level of theory. For benzene, the geometry of the dication differs somewhat from that of the cation, and, as a result, the vertical second ionization energy is 17 kcal mol^{-1} larger than the adiabatic. However, this difference is reduced to 5 kcal mol^{-1} for circumcoronene. Thus, the excess energy deposited in the dication due to the differences in geometry between the cation and dication is relatively small. Therefore, when the dication is formed by ionization of the cation, the internal energy is small. This is consistent with the observation of dications under soft ionization conditions.

We now consider the possible reactions of the benzene dication. Our results are summarized in Figures 1–4. To make it easy to find a specific reaction, they are denoted "x.y,"
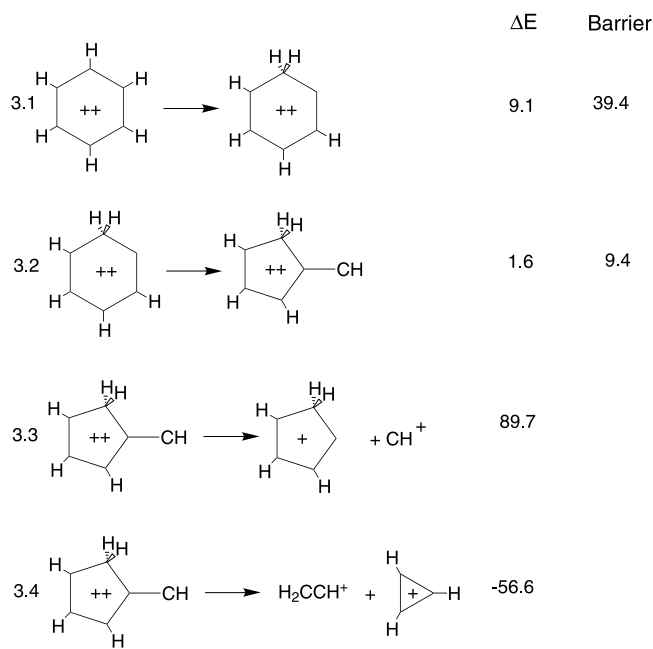
FIG. 3.—Barriers and heats of reactions in kcal mol^{-1}.

FIG. 4.—Barriers and heats of reactions in kcal mol^{-1}.

where x is the figure number and y is the reaction number in that figure.

As was pointed out by Krogh-Jespersen (1991), the most stable form of $C_6H_6^{+2}$ has C_{5v} symmetry and corresponds to a CH group along the C_5 axis of a C_5H_5 group. However, for a multiple-ring PAH molecule, the six-membered ring form is expected to be more stable than the five-membered ring species, and therefore we take the six-membered distorted benzene-like structure as our starting point.

While we find a singlet ground state for $C_6H_6^{+2}$, as did Krogh-Jespersen (1991), we should note that for the benzene-like structure, the triplet state is 3.05 kcal mol^{-1} below the singlet state at the B3LYP/6-31G* level of theory. However, at the CCSD(T) level using the large cc-pVTZ basis set, the singlet state is 2.2 kcal mol^{-1} below the triplet. Thus, higher levels of theory show that the ground state is a singlet despite the ordering at the B3LYP/6-31G* level. In addition, we find at the B3LYP/4-31G level that the triplet is 4.91 kcal mol^{-1} below the singlet for the benzene dication but only 2.2 kcal mol^{-1} lower for the circumcoronene dication. Thus, increasing the size of the molecule favors the singlet state relative to the triplet. Therefore, we believe that the singlet state is the ground state for the larger PAH dications, as well as for the benzene dication. Since spin-orbit coupling is not expected to be important for $C_6H_6^{+2}$, we consider the singlet surfaces for all reactions presented here.

In Figure 1 we show the several reactions that are exothermic or weakly endothermic. We have studied these reactions in detail, and we are unable to find a transition state connecting the reactants and products. We therefore believe that the barrier heights for these reactions are very large and that these reactions are not practical despite their apparently favorable reaction energies. We do not consider these reactions further.

The loss of an H$^+$ and/or H is an endothermic process (see reactions 2.1 and 2.2). While we have not computed the barrier for the loss of an H, we do not expect this barrier to be significantly larger than the endothermicity. The loss of H$^+$, which results in the formation of two ions, has a barrier due to
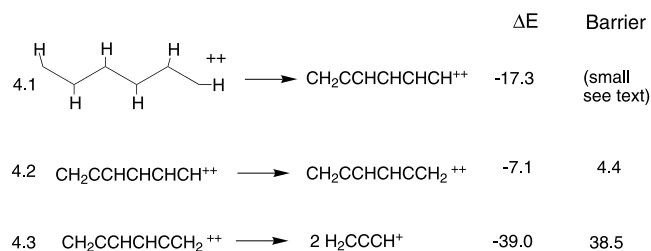
Coulomb repulsion at larger r-values. Unfortunately, we are unable to find the transition state; all of our attempts result in finding the barrier for an H shift (see reaction 3.1). If we fix the C(para)-C-H angle to 180° and optimize all other parameters as a function of the C-H distance, we find a barrier of 109 kcal mol^{-1}. Clearly, the loss of an H$^+$ requires a significant amount of energy. The loss of an H or H$^+$ by the dication requires about the same amount of energy as losing an H atom in the neutral or cation.

The rearrangement to form the C_{5v} structure (reaction 2.3) has a barrier of 26.4 kcal mol^{-1} and is exothermic by 3.0 kcal mol^{-1}. This is consistent with Krogh-Jespersen (1991), who also found the C_{5v} structure to be the most stable. We illustrate a typical transition state in Figure 5, in which we show the transition state connecting ring and C_{5v} forms of $C_6H_6^{+2}$, as well as the reactant and product. The loss of the CH$^+$ from this structure is endothermic by 75.6 kcal mol^{-1} (see reaction 2.4), but like the loss of H$^+$, this reaction forms two cations, and therefore there is a significant barrier. This rearrangement and loss of CH$^+$ is a mechanism for the formation of a five-membered ring. In a larger PAH, the barrier would be expected to increase and the reaction to become endothermic, since distorting the neighboring rings would make the reaction less favorable. Thus, the formation of the five-membered ring appears less favorable than the loss of an H$^+$.

Another process that we studied was the ring opening (reaction 2.5), which was found to have a barrier that is somewhat lower than the loss of H$^+$ or the five-membered ring rearrangement followed by the loss of CH$^+$. As with the formation of the five-membered ring, we believe that the ring opening requires more energy for larger PAHs due to the energy needed to deform the neighboring rings.

We have found a second mechanism for the formation of a five-membered ring and the loss of CH$^+$; these are reactions 3.1–3.3. The first step is an H shift, which has a modest barrier. The second step is the formation of the five-membered ring, which is only slightly endothermic and has a small barrier. The final step is the loss of the CH$^+$. Thus, there appear to be two viable mechanisms for the formation of five-membered rings for the dications. However, both of these mechanisms appear to have larger barriers and are more complicated than the loss of H$^+$. Finally, we note that we tried fragmenting the five-membered ring product of reaction 3.2 into two C_3 species, and while the process is exothermic, we were unable to find a transition state for the process, so we do not believe that such a fragmentation path is important.

Since C_2, C_3, and C_4 fragments are found in the high-energy experiments, we considered how such species would be formed if direct processes, such as those in Figure 1, were not practical. As shown in reaction 2.5, the ring opening seems like a possible path, and we therefore investigate the fragmentation of the linear species. Reaction 4.1 shows an H shift. We find
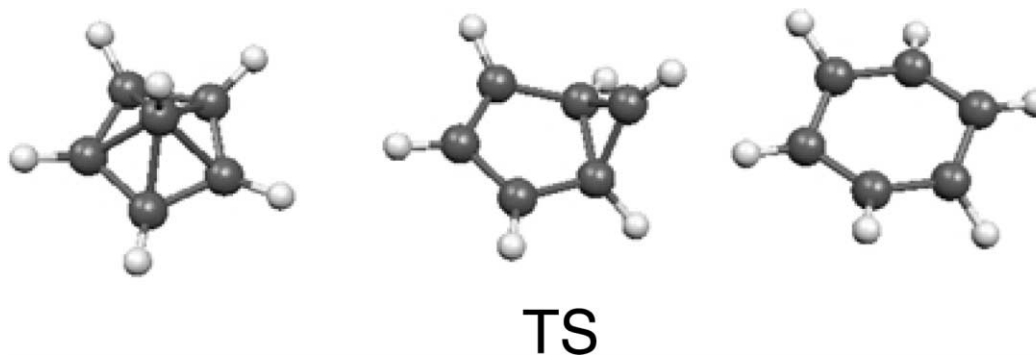
Fig. 5.—Equilibrium structures for the ring and C_{5v} forms of $C_6H_6^{+2}$, as well as the transition state connecting them. [*See the electronic edition of the Journal for a color version of this figure.*]

this reaction to be exothermic. The reaction path seems to be more complex than might be assumed. We found a transition state for the reaction that shifts the H to the C-C bond midpoint. This bond midpoint minima is only 1.3 kcal mol^{-1} below the reactant. While the transition state is marginally above the reactant without zero-point energy, with zero-point energy the transition state is 0.6 kcal mol^{-1} below the reactant. The potential energy surface appears to have several bumps, and we located additional stationary points between the H at the bond midpoint and the products. While we have not fully mapped out the path connecting the reactants and products, it appears that the barrier, if one exists, is very small. The H shift on the opposite end of the chain (see reaction 4.2) has a very small barrier and is slightly exothermic. This species can divide (see reaction 4.3) into two C_3 species with an exothermic reaction and a modest barrier.

Our calculations suggest that the most likely process for a PAH dication with excess thermal energy is the loss of an H$^+$. Because of the large excess of H to C, one would expect that the cation that was formed would react with an H atom or H$_2$ molecule to reform the starting cation. We have also found two mechanisms for the formation of five-membered rings. In larger symmetric PAHs, these processes might not be too favorable, since the neighboring rings would resist the formation of the five-membered ring. For less symmetric PAH species, the dication appears to offer a mechanism for the formation of five-membered rings. Finally, we note that our calculations show that a ring opening requires about the same energy as the loss of H$^+$ or the formation of a five-membered ring. Once the chain forms, we suspect that this is the main mechanism by which the C_2, C_3, and C_4 fragments form. Thus, the fragmentation observed in high-energy experiments can occur by way of a linear system, even if the direct fragmentation mechanisms shown in Figure 1 are unfavorable. The calcu-

lations show that $C_6H_6^{+2}$ is kinetically stable, even if $C_6H_6^{+2}$ is higher in energy than several of the possible products. On the basis of these results, we conclude that PAH dications should be included in astrophysical models.

4. CONCLUSIONS

While the benzene dication energy is significantly above that of two fragment cations, we are unable to find any low-energy paths to fragmentations; this is consistent with the observation that soft ionization experiments form dications. Even the loss of H$^+$, which is endothermic by 50 kcal mol^{-1}, has a barrier of about 100 kcal mol^{-1}. While benzene itself is not of much importance in interstellar chemistry, its stability does offer some insight into the stability of PAH dications, since the fragmentation paths for the PAHs are expected to be equal to or larger than those for the benzene dication. On the basis of results for $C_6H_6^{+2}$, we conclude that while the PAH dications will have a much shorter lifetime than the neutrals or cations, they will still exist for reasonable times. Because of the number of H atoms, it is expected that after the loss of the H$^+$, the parent cation will be regenerated in a subsequent reaction with an H atom. Thus, one fate of the dications is to absorb a photon and dissociate, thereby converting radiation into thermal energy. It is also possible that they will absorb a photon and radiate in the IR, like the neutrals and cations. Finally, we note that dications could be a route for forming five-membered rings.

REFERENCES

Allain, T., Leach, S., & Sedlmayr, E. 1996a, A&A, 305, 602
———. 1996b, A&A, 305, 616
Allamandola, L. J., Tielens, A. G. G. M., & Barker, J. R. 1989, ApJS, 71, 733
Bakes, E. L. O., & Tielens, A. G. G. M. 1994, ApJ, 427, 822
Bakes, E. L. O., Tielens, A. G. G. M., & Bauschlicher, C. W. 2001a, ApJ, 556, 501
Bakes, E. L. O., Tielens, A. G. G. M., Bauschlicher, C. W., Hudgins, D. M., & Allamandola, L. J. 2001b, ApJ, 560, 261
Bauschlicher, C. W., & Bakes, E. L. O. 2000, Chem. Phys., 262, 285
Bauschlicher, C. W., & Langhoff, S. R. 1989, Chem. Phys. Lett., 161, 383
Becke, A. D. 1993, J. Chem. Phys., 98, 5648
Cook, D. J., & Saykally, R. J. 1998, ApJ, 493, 793
DeFrees, D. J., Miller, M. D., Talbi, D., Pauzat, F., & Ellinger, Y. J. 1993, ApJ, 408, 530

Draine, B. T. 1978, ApJS, 36, 595
Frisch, M. J., Pople, J. A., & Binkley, J. S. 1984, J. Chem. Phys., 80, 3265
Frisch, M. J., et al. 1998, Gaussian 98 (version A.9; Pittsburgh: Gaussian)
Huang, Y., & Freiser, B. S. 1988, J. Am. Chem. Soc., 110, 4435
Hudgins, D. M., & Allamandola, L. J. 1999, ApJ, 513, L69
Hudgins, D. M., Bauschlicher, C. W., & Allamandola, L. J. 2001, Spectrochim. Acta A, 57, 907
Joblin, C., d'Hendecourt, L., Léger, A., & Défourneau, D. 1994, A&A, 281, 923
Kendall, R. A., Dunning, T. H., & Harrison, R. J. 1992, J. Chem. Phys., 96, 6796
Krogh-Jespersen, K. 1991, J. Am. Chem. Soc., 113, 417
Langhoff, S. R. 1996, J. Phys. Chem., 100, 2819
Leach, S. 1987, J. Electron. Spectrosc. Relativ. Phenomena, 41, 427

Leach, S., Eland, J. H. D., & Price, S. D. 1989, J. Phys. Chem., 93, 7575

Ledingham, K. W. D., et al. 1999, J. Phys. Chem., 103, 2952

Piest, H., von Helden, G., & Meijer, G. 1999, ApJ, 520, L75

Puget, J. L., & Léger, A. 1989, ARA&A, 27, 161

Raghavachari, K., Trucks, G. W., Pople, J. A., & Head-Gordon, M. 1989, Chem. Phys. Lett., 157, 479

Schutte, W. A., Tielens, A. G. G. M., & Allamandola, L. J. 1993, ApJ, 415, 397

Stephens, P. J., Devlin, F. J., Chabalowski, C. F., & Frisch, M. J. 1994, J. Phys. Chem., 98, 11623

Szczepanski, J., & Vala, M. 1993, Nature, 363, 699

Werner, H. J., & Knowles, P. J. 2002, MOLPRO (version 2002.1; Birmingham: Univ. Birmingham)