

文章编号 1000-5013(2001) 01-040-04

丙二烯分子结构的量子化学从头计算

黄贻深 吴季怀

(华侨大学材料科学与工程学院, 泉州 362011)

摘要 采用 PSHONDO-SCF 全电子从头计算程序, 对丙二烯分子的两种不同对称性构型的电子结构进行计算. 结果表明丙二烯分子, 采用 D_{2d} 对称结构比 D_{2h} 对称结构更稳定. 丙二烯分子 (D_{2d}) 的电子结构: (1) 总能量为 $-5.042\,946\,20 \times 10^{-16}$ J, 前线轨道 HOMO 为 $E(2e) = -1.640\,192\,56 \times 10^{-18}$ J, LUMO 为 $E(3e) = 7.661\,105\,24 \times 10^{-19}$ J; (2) 键级直接相键连的 C-H 为 0.381 4, C=C 为 0.677 11; (3) 电荷分布—— $C_{(1)}$ 为 $-0.175\,8$, $C_{(2)}$ 和 $C_{(3)}$ 均为 $-0.224\,8$, H 为 $0.156\,4$.
关键词 量子化学计算, 丙二烯, 全电子从头计算

中图分类号 O 641.12⁺ 1 : O 623.122 : O 621.13

文献标识码 A

关于丙二烯的分子结构, 通常都是认为两个 C=C 双键中的 π 键处于相互垂直位置, 因而不发生共轭. 4 个 H 原子不在同一平面上, 因此应是属于 D_{2d} 对称. 但也有认为丙二烯分子可属于 D_{2h} 对称, 4 个原子处于同一平面, 两个 C=C 双键可以发生共轭, 形成 π^4 结构. 为了回答哪一种看法更合理的问题, 本文采用目前量子化学计算中公认的最精确的全电子从头计算法, 对丙二烯分子的两种不同对称性构型进行计算, 以便对丙二烯分子的结构提供一些理论依据. 本计算采用大连化物所调试的 PSHONDO 程序. 该程序是以 HONDO 程序为基础发展而来的, 是一种 SCF 自洽场从头计算程序. 其主要特点是在计算积分和 SCF 自洽场迭代过程中采用了点群对称性, 因而使计算程序量较小, 计算速度较快, 计算的精确度高.

1 计算方法和计算参数选择

在 LCAO-SCF 理论中, 分子轨道可以表示为 $\psi_i = \sum_{\mu} C_{\mu i} \Phi_{\mu}$, 其中 Φ_{μ} 为基函数, $C_{\mu i}$ 为组合系数. 基函数的选择对于 SCF 计算结果至关重要. 在现在的量子化学计算中, 一种常用做法是用一简缩的高斯函数进行拟合. 高斯函数形式为

$$g_s(\alpha, r) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2), \quad g_{px}(\alpha, r) = (128\alpha^5/\pi^3)^{1/4} x \exp(-\alpha r^2).$$

在用高斯函数进行拟合时, 采用所谓“分裂价基”的基组效果更好. 即每个内壳层轨道用

$$\text{一个函数表示, 而对于价壳层轨道则采用两个函数表示为 } \Phi_s(r) = \sum_{k=1}^{N_1} d_{1s,k} g_s(\alpha_{1k}, r), \quad \Phi_s^{\text{②}}(r) = \sum_{k=1}^{N_1} d_{2s,k} g_s(\alpha_{2k}, r), \quad \Phi_s^{\text{③}}(r) = \sum_{k=1}^{N_1} d_{3s,k} g_s(\alpha_{3k}, r), \quad \Phi_{px}^{\text{④}}(r) = \sum_{k=1}^{N_1} d_{4px,k} g_{px}(\alpha_{4k}, r), \quad \Phi_{px}^{\text{⑤}}(r) = \sum_{k=1}^{N_1} d_{5px,k} g_{px}(\alpha_{5k}, r), \quad \Phi_{px}^{\text{⑥}}(r) = \sum_{k=1}^{N_1} d_{6px,k} g_{px}(\alpha_{6k}, r), \quad \Phi_{px}^{\text{⑦}}(r) = \sum_{k=1}^{N_1} d_{7px,k} g_{px}(\alpha_{7k}, r), \quad \Phi_{px}^{\text{⑧}}(r) = \sum_{k=1}^{N_1} d_{8px,k} g_{px}(\alpha_{8k}, r), \quad \Phi_{px}^{\text{⑨}}(r) = \sum_{k=1}^{N_1} d_{9px,k} g_{px}(\alpha_{9k}, r), \quad \Phi_{px}^{\text{⑩}}(r) = \sum_{k=1}^{N_1} d_{10px,k} g_{px}(\alpha_{10k}, r), \quad \Phi_{px}^{\text{⑪}}(r) = \sum_{k=1}^{N_1} d_{11px,k} g_{px}(\alpha_{11k}, r), \quad \Phi_{px}^{\text{⑫}}(r) = \sum_{k=1}^{N_1} d_{12px,k} g_{px}(\alpha_{12k}, r), \quad \Phi_{px}^{\text{⑬}}(r) = \sum_{k=1}^{N_1} d_{13px,k} g_{px}(\alpha_{13k}, r), \quad \Phi_{px}^{\text{⑭}}(r) = \sum_{k=1}^{N_1} d_{14px,k} g_{px}(\alpha_{14k}, r), \quad \Phi_{px}^{\text{⑮}}(r) = \sum_{k=1}^{N_1} d_{15px,k} g_{px}(\alpha_{15k}, r), \quad \Phi_{px}^{\text{⑯}}(r) = \sum_{k=1}^{N_1} d_{16px,k} g_{px}(\alpha_{16k}, r), \quad \Phi_{px}^{\text{⑰}}(r) = \sum_{k=1}^{N_1} d_{17px,k} g_{px}(\alpha_{17k}, r), \quad \Phi_{px}^{\text{⑱}}(r) = \sum_{k=1}^{N_1} d_{18px,k} g_{px}(\alpha_{18k}, r), \quad \Phi_{px}^{\text{⑲}}(r) = \sum_{k=1}^{N_1} d_{19px,k} g_{px}(\alpha_{19k}, r), \quad \Phi_{px}^{\text{⑳}}(r) = \sum_{k=1}^{N_1} d_{20px,k} g_{px}(\alpha_{20k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{21px,k} g_{px}(\alpha_{21k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{22px,k} g_{px}(\alpha_{22k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{23px,k} g_{px}(\alpha_{23k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{24px,k} g_{px}(\alpha_{24k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{25px,k} g_{px}(\alpha_{25k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{26px,k} g_{px}(\alpha_{26k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{27px,k} g_{px}(\alpha_{27k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{28px,k} g_{px}(\alpha_{28k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{29px,k} g_{px}(\alpha_{29k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{30px,k} g_{px}(\alpha_{30k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{31px,k} g_{px}(\alpha_{31k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{32px,k} g_{px}(\alpha_{32k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{33px,k} g_{px}(\alpha_{33k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{34px,k} g_{px}(\alpha_{34k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{35px,k} g_{px}(\alpha_{35k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{36px,k} g_{px}(\alpha_{36k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{37px,k} g_{px}(\alpha_{37k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{38px,k} g_{px}(\alpha_{38k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{39px,k} g_{px}(\alpha_{39k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{40px,k} g_{px}(\alpha_{40k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{41px,k} g_{px}(\alpha_{41k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{42px,k} g_{px}(\alpha_{42k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{43px,k} g_{px}(\alpha_{43k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{44px,k} g_{px}(\alpha_{44k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{45px,k} g_{px}(\alpha_{45k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{46px,k} g_{px}(\alpha_{46k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{47px,k} g_{px}(\alpha_{47k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{48px,k} g_{px}(\alpha_{48k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{49px,k} g_{px}(\alpha_{49k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{50px,k} g_{px}(\alpha_{50k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{51px,k} g_{px}(\alpha_{51k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{52px,k} g_{px}(\alpha_{52k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{53px,k} g_{px}(\alpha_{53k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{54px,k} g_{px}(\alpha_{54k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{55px,k} g_{px}(\alpha_{55k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{56px,k} g_{px}(\alpha_{56k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{57px,k} g_{px}(\alpha_{57k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{58px,k} g_{px}(\alpha_{58k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{59px,k} g_{px}(\alpha_{59k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{60px,k} g_{px}(\alpha_{60k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{61px,k} g_{px}(\alpha_{61k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{62px,k} g_{px}(\alpha_{62k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{63px,k} g_{px}(\alpha_{63k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{64px,k} g_{px}(\alpha_{64k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{65px,k} g_{px}(\alpha_{65k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{66px,k} g_{px}(\alpha_{66k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{67px,k} g_{px}(\alpha_{67k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{68px,k} g_{px}(\alpha_{68k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{69px,k} g_{px}(\alpha_{69k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{70px,k} g_{px}(\alpha_{70k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{71px,k} g_{px}(\alpha_{71k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{72px,k} g_{px}(\alpha_{72k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{73px,k} g_{px}(\alpha_{73k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{74px,k} g_{px}(\alpha_{74k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{75px,k} g_{px}(\alpha_{75k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{76px,k} g_{px}(\alpha_{76k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{77px,k} g_{px}(\alpha_{77k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{78px,k} g_{px}(\alpha_{78k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{79px,k} g_{px}(\alpha_{79k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{80px,k} g_{px}(\alpha_{80k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{81px,k} g_{px}(\alpha_{81k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{82px,k} g_{px}(\alpha_{82k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{83px,k} g_{px}(\alpha_{83k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{84px,k} g_{px}(\alpha_{84k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{85px,k} g_{px}(\alpha_{85k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{86px,k} g_{px}(\alpha_{86k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{87px,k} g_{px}(\alpha_{87k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{88px,k} g_{px}(\alpha_{88k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{89px,k} g_{px}(\alpha_{89k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{90px,k} g_{px}(\alpha_{90k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{91px,k} g_{px}(\alpha_{91k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{92px,k} g_{px}(\alpha_{92k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{93px,k} g_{px}(\alpha_{93k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{94px,k} g_{px}(\alpha_{94k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{95px,k} g_{px}(\alpha_{95k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{96px,k} g_{px}(\alpha_{96k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{97px,k} g_{px}(\alpha_{97k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{98px,k} g_{px}(\alpha_{98k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{99px,k} g_{px}(\alpha_{99k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{100px,k} g_{px}(\alpha_{100k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{101px,k} g_{px}(\alpha_{101k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{102px,k} g_{px}(\alpha_{102k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{103px,k} g_{px}(\alpha_{103k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{104px,k} g_{px}(\alpha_{104k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{105px,k} g_{px}(\alpha_{105k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{106px,k} g_{px}(\alpha_{106k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{107px,k} g_{px}(\alpha_{107k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{108px,k} g_{px}(\alpha_{108k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{109px,k} g_{px}(\alpha_{109k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{110px,k} g_{px}(\alpha_{110k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{111px,k} g_{px}(\alpha_{111k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{112px,k} g_{px}(\alpha_{112k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{113px,k} g_{px}(\alpha_{113k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{114px,k} g_{px}(\alpha_{114k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{115px,k} g_{px}(\alpha_{115k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{116px,k} g_{px}(\alpha_{116k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{117px,k} g_{px}(\alpha_{117k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{118px,k} g_{px}(\alpha_{118k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{119px,k} g_{px}(\alpha_{119k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{120px,k} g_{px}(\alpha_{120k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{121px,k} g_{px}(\alpha_{121k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{122px,k} g_{px}(\alpha_{122k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{123px,k} g_{px}(\alpha_{123k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{124px,k} g_{px}(\alpha_{124k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{125px,k} g_{px}(\alpha_{125k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{126px,k} g_{px}(\alpha_{126k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{127px,k} g_{px}(\alpha_{127k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{128px,k} g_{px}(\alpha_{128k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{129px,k} g_{px}(\alpha_{129k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{130px,k} g_{px}(\alpha_{130k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{131px,k} g_{px}(\alpha_{131k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{132px,k} g_{px}(\alpha_{132k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{133px,k} g_{px}(\alpha_{133k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{134px,k} g_{px}(\alpha_{134k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{135px,k} g_{px}(\alpha_{135k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{136px,k} g_{px}(\alpha_{136k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{137px,k} g_{px}(\alpha_{137k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{138px,k} g_{px}(\alpha_{138k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{139px,k} g_{px}(\alpha_{139k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{140px,k} g_{px}(\alpha_{140k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{141px,k} g_{px}(\alpha_{141k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{142px,k} g_{px}(\alpha_{142k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{143px,k} g_{px}(\alpha_{143k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{144px,k} g_{px}(\alpha_{144k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{145px,k} g_{px}(\alpha_{145k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{146px,k} g_{px}(\alpha_{146k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{147px,k} g_{px}(\alpha_{147k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{148px,k} g_{px}(\alpha_{148k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{149px,k} g_{px}(\alpha_{149k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{150px,k} g_{px}(\alpha_{150k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{151px,k} g_{px}(\alpha_{151k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{152px,k} g_{px}(\alpha_{152k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{153px,k} g_{px}(\alpha_{153k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{154px,k} g_{px}(\alpha_{154k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{155px,k} g_{px}(\alpha_{155k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{156px,k} g_{px}(\alpha_{156k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{157px,k} g_{px}(\alpha_{157k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{158px,k} g_{px}(\alpha_{158k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{159px,k} g_{px}(\alpha_{159k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{160px,k} g_{px}(\alpha_{160k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{161px,k} g_{px}(\alpha_{161k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{162px,k} g_{px}(\alpha_{162k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{163px,k} g_{px}(\alpha_{163k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{164px,k} g_{px}(\alpha_{164k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{165px,k} g_{px}(\alpha_{165k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{166px,k} g_{px}(\alpha_{166k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{167px,k} g_{px}(\alpha_{167k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{168px,k} g_{px}(\alpha_{168k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{169px,k} g_{px}(\alpha_{169k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{170px,k} g_{px}(\alpha_{170k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{171px,k} g_{px}(\alpha_{171k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{172px,k} g_{px}(\alpha_{172k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{173px,k} g_{px}(\alpha_{173k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{174px,k} g_{px}(\alpha_{174k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{175px,k} g_{px}(\alpha_{175k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{176px,k} g_{px}(\alpha_{176k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{177px,k} g_{px}(\alpha_{177k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d_{178px,k} g_{px}(\alpha_{178k}, r), \quad \Phi_{px}^{\text{㉙}}(r) = \sum_{k=1}^{N_1} d_{179px,k} g_{px}(\alpha_{179k}, r), \quad \Phi_{px}^{\text{㉚}}(r) = \sum_{k=1}^{N_1} d_{180px,k} g_{px}(\alpha_{180k}, r), \quad \Phi_{px}^{\text{㉛}}(r) = \sum_{k=1}^{N_1} d_{181px,k} g_{px}(\alpha_{181k}, r), \quad \Phi_{px}^{\text{㉜}}(r) = \sum_{k=1}^{N_1} d_{182px,k} g_{px}(\alpha_{182k}, r), \quad \Phi_{px}^{\text{㉝}}(r) = \sum_{k=1}^{N_1} d_{183px,k} g_{px}(\alpha_{183k}, r), \quad \Phi_{px}^{\text{㉞}}(r) = \sum_{k=1}^{N_1} d_{184px,k} g_{px}(\alpha_{184k}, r), \quad \Phi_{px}^{\text{㉟}}(r) = \sum_{k=1}^{N_1} d_{185px,k} g_{px}(\alpha_{185k}, r), \quad \Phi_{px}^{\text{㊱}}(r) = \sum_{k=1}^{N_1} d_{186px,k} g_{px}(\alpha_{186k}, r), \quad \Phi_{px}^{\text{㊲}}(r) = \sum_{k=1}^{N_1} d_{187px,k} g_{px}(\alpha_{187k}, r), \quad \Phi_{px}^{\text{㊳}}(r) = \sum_{k=1}^{N_1} d_{188px,k} g_{px}(\alpha_{188k}, r), \quad \Phi_{px}^{\text{㊴}}(r) = \sum_{k=1}^{N_1} d_{189px,k} g_{px}(\alpha_{189k}, r), \quad \Phi_{px}^{\text{㊵}}(r) = \sum_{k=1}^{N_1} d_{190px,k} g_{px}(\alpha_{190k}, r), \quad \Phi_{px}^{\text{㊶}}(r) = \sum_{k=1}^{N_1} d_{191px,k} g_{px}(\alpha_{191k}, r), \quad \Phi_{px}^{\text{㊷}}(r) = \sum_{k=1}^{N_1} d_{192px,k} g_{px}(\alpha_{192k}, r), \quad \Phi_{px}^{\text{㊸}}(r) = \sum_{k=1}^{N_1} d_{193px,k} g_{px}(\alpha_{193k}, r), \quad \Phi_{px}^{\text{㊹}}(r) = \sum_{k=1}^{N_1} d_{194px,k} g_{px}(\alpha_{194k}, r), \quad \Phi_{px}^{\text{㊺}}(r) = \sum_{k=1}^{N_1} d_{195px,k} g_{px}(\alpha_{195k}, r), \quad \Phi_{px}^{\text{㊻}}(r) = \sum_{k=1}^{N_1} d_{196px,k} g_{px}(\alpha_{196k}, r), \quad \Phi_{px}^{\text{㊼}}(r) = \sum_{k=1}^{N_1} d_{197px,k} g_{px}(\alpha_{197k}, r), \quad \Phi_{px}^{\text{㊽}}(r) = \sum_{k=1}^{N_1} d_{198px,k} g_{px}(\alpha_{198k}, r), \quad \Phi_{px}^{\text{㊾}}(r) = \sum_{k=1}^{N_1} d_{199px,k} g_{px}(\alpha_{199k}, r), \quad \Phi_{px}^{\text{㊿}}(r) = \sum_{k=1}^{N_1} d_{200px,k} g_{px}(\alpha_{200k}, r), \quad \Phi_{px}^{\text{㉑}}(r) = \sum_{k=1}^{N_1} d_{201px,k} g_{px}(\alpha_{201k}, r), \quad \Phi_{px}^{\text{㉒}}(r) = \sum_{k=1}^{N_1} d_{202px,k} g_{px}(\alpha_{202k}, r), \quad \Phi_{px}^{\text{㉓}}(r) = \sum_{k=1}^{N_1} d_{203px,k} g_{px}(\alpha_{203k}, r), \quad \Phi_{px}^{\text{㉔}}(r) = \sum_{k=1}^{N_1} d_{204px,k} g_{px}(\alpha_{204k}, r), \quad \Phi_{px}^{\text{㉕}}(r) = \sum_{k=1}^{N_1} d_{205px,k} g_{px}(\alpha_{205k}, r), \quad \Phi_{px}^{\text{㉖}}(r) = \sum_{k=1}^{N_1} d_{206px,k} g_{px}(\alpha_{206k}, r), \quad \Phi_{px}^{\text{㉗}}(r) = \sum_{k=1}^{N_1} d_{207px,k} g_{px}(\alpha_{207k}, r), \quad \Phi_{px}^{\text{㉘}}(r) = \sum_{k=1}^{N_1} d$$

$g_{\text{px}}(\alpha^{2k''}, r)$. 对 H 原子, 因没有内壳层, 可表示 $\Phi_s^{\text{H}}(r) = \sum_{K=1}^{N_1^{\text{H}}} d_K^{\text{H}} g_s(\alpha_K^{\text{H}}, r)$, $\Phi_s^{\text{C}}(r) = \sum_{K=1}^{N_1^{\text{C}}} d_K^{\text{C}} g_s(\alpha_K^{\text{C}}, r)$. 在本文计算中, 包含 3 个 C 原子和 4 个 H 原子. 每个 C 原子选择了 9 个基函数, 其中 1s 轨道的 1 个基函数 Φ_{1s} , 2s 轨道的 2 个基函数 Φ_{2s}^{H} 和 Φ_{2s}^{C} , 2p 轨道的 6 个基函数为 $\Phi_{2\text{px}}^{\text{H}}$, $\Phi_{2\text{py}}^{\text{H}}$, $\Phi_{2\text{pz}}^{\text{H}}$, $\Phi_{2\text{px}}^{\text{C}}$, $\Phi_{2\text{py}}^{\text{C}}$, $\Phi_{2\text{pz}}^{\text{C}}$. 每个 H 原子的 2 个基函数 Φ_{2s}^{H} 和 $\Phi_{2p_z}^{\text{H}}$. 总有共 35 个基函数. 对于 C 原子选择 $N_1^{\text{C}} = 4$, $N_2^{\text{C}} = 3$, $N_3^{\text{C}} = 1$. 对 H 原子选择 $N_1^{\text{H}} = 3$, $N_2^{\text{H}} = 1$. 这种基组又称为 4-31 基组. 计算中所采用的参数, 见文献 [1].

2 计算结果与讨论

2.1 构型优化

依据实验数据, 对丙二烯分子两种不同对称性构型(图 1), 进行优化计算. 优化计算中, 角度变化步长为 1° ; 键长变化步长为 $0.1 \sim 1.0$ pm. 计算结果见表 1, 2. 优化后的结构参数见表 3. 优化计算结果, $R_{\text{C}=\text{C}}$ 键长与文献 [3,3] 所提供数据略有出入.

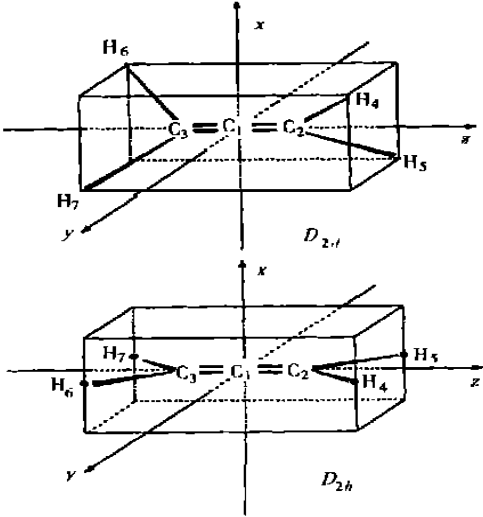


图 1 丙二烯分子的构型

表 1 D_{2d} 对称丙二烯结构优化计算结果

$r_{\text{C}=\text{C}}/\text{pm}$	$r_{\text{C}=\text{H}}/\text{pm}$	$\text{HCH}/(^{\circ})$	$E_{\text{总}}/\text{fJ}$	$r_{\text{C}=\text{C}}/\text{pm}$	$r_{\text{C}=\text{H}}/\text{pm}$	$\text{HCH}/(^{\circ})$	$E_{\text{总}}/\text{fJ}$
128	110.0	109	- 0.504 274 456	129	108.2	109	- 0.504 279 462
129	110.0	109	- 0.504 275 782	129	108.0	109	- 0.504 279 444
130	110.0	109	- 0.504 274 548	129	108.2	109	- 0.504 279 401
133	110.0	109	- 0.504 256 883	129	108.2	114	- 0.504 292 653
129	108.5	109	- 0.504 279 369	129	108.2	117	- 0.504 294 620
129	108.4	109	- 0.504 279 422	129	108.2	118	- 0.504 294 307
129	108.3	109	- 0.504 279 452	129	108.2	119	- 0.504 293 513

表 2 D_{2h} 对称丙二烯结构优化计算结果

$r_{\text{C}=\text{C}}/\text{pm}$	$r_{\text{C}=\text{H}}/\text{pm}$	$\text{HCH}/(^{\circ})$	$E_{\text{总}}/\text{fJ}$	$r_{\text{C}=\text{C}}/\text{pm}$	$r_{\text{C}=\text{H}}/\text{pm}$	$\text{HCH}/(^{\circ})$	$E_{\text{总}}/\text{fJ}$
129	108.7	118	- 0.503 345 446	134	108.7	115	- 0.503 383 926
130	108.7	118	- 0.503 355 303	134	108.7	113	- 0.503 389 282
131	108.7	118	- 0.503 362 704	134	108.7	110	- 0.503 392 660
132	108.7	118	- 0.503 367 768	134	108.7	109	- 0.503 392 517
133	108.7	118	- 0.503 370 613	134	108.7	108	- 0.503 391 735
134	108.7	118	- 0.503 371 359	134	108.7	106	- 0.503 388 207
135	108.7	118	- 0.503 370 113	131	108.7	109	- 0.503 389 327
136	108.7	118	- 0.503 366 972	132	108.7	109	- 0.503 392 556
134	108.7	120	- 0.593 360 031	133	108.7	109	- 0.503 393 582
134	108.7	119	- 0.503 365 985	135	108.7	109	- 0.503 389 479
134	108.7	117	- 0.503 376 142				

表 3 丙二烯两种构型优化结构参数

项 目	$r_{C=C}/\text{pm}$	r_{C-H}/pm	HCH/($^{\circ}$)	$E_{\text{总}}/\text{J}$
D_{2d} 对称性	129.0	108.6	117	$-5.042\,946\,20\times 10^{-16}$
D_{2h} 对称性	133.0	108.7	109	$-5.033\,935\,82\times 10^{-16}$
文献值	130.7 ^[1] , 133.0 ^[3]	108.7	—	—

2.2 丙二烯分子的电子结构

根据结构优化计算获得丙二烯两种不同构型的结构参数,用 PSHONDO 全电子从头计算程序,计算两种不同对称构型丙二烯分子的电子结构(表 4).表中 $E_{\text{总}}$ 为总能量, E 为前线轨道能量, $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, C(1) - C(2) ~ H(6) - H(7) 为键级, C(2) ~ H(7) 为电荷.

表 4 丙二烯两种构型电子结构

项 目	D_{2d} 对称	D_2 对称
总能量/fJ	- 0.504 294 620	- 0.503 393 582
$E_{\text{HOMO}}/\text{fJ}$	- 0.001 640 192 56	- 0.000 886 501 98
$E_{\text{LUMO}}/\text{fJ}$	0.000 766 110 52	- 0.000 023 532 55
$\Delta E/\text{fJ}$	0.002 406 303 80	0.000 862 965 08
C(1) - C(2), C(1) - C(3)	0.677 11	0.631 9
C(2) - C(3)	- 0.044 5	- 0.018 7
C(1) - H(4), C(1) - H(5)	- 0.030 7	- 0.081 9
C(1) - H(6), C(1) - H(7)	- 0.030 7	- 0.081 9
C(2) - H(4), C(2) - H(5)	0.381 4	0.352 0
C(2) - H(6), C(2) - H(7)	0.000 2	0.001 2
C(3) - H(4), C(3) - H(5)	0.000 2	0.001 2
项 目	D_{2h} 对称	D_2 对称
C(3) - H(6), C(3) - H(7)	0.381 4	0.352 0
H(4) - H(5)	- 0.028 2	- 0.113 7
H(4) - H(6)	- 0.000 1	- 0.003 2
H(4) - H(7)	- 0.000 1	- 0.001 6
H(5) - H(6)	- 0.000 1	—
H(5) - H(7)	- 0.000 1	—
H(6) - H(7)	- 0.022 8	- 0.113 7
C(1)	- 0.175 8	- 0.640 4
C(2), C(3)	- 0.224 8	0.104 6
H(4), H(5), H(6), H(7)	0.156 4	0.107 9

(1) D_{2d} 对称构型比 D_{2h} 对称构型的分子总能量更低,前线轨道能级差较大, C=C 及 C-H 键级较大. 而且,在 D_{2d} 对称构型中, H 原子之间的排斥作用比 D_{2h} 构型中的小很多. 由此表明,采用 D_{2d} 对称构型比 D_{2h} 对称构型更稳定些. (2) 两种构型分子中,电荷分布有明显不同. 在 D_{2d} 对称构型中, 3 个 C 原子均带负电荷, 而且每个 H 原子所带正电荷也较大些. 而在 D_{2h} 构型中, $C^{[1]}$ 带负电荷而 $C^{[2]}$ 及 $C^{[3]}$ 均带正电荷. 由于在 Mulliken 集居分析中,对原子间的重迭集居的处理,是将其平均分配给原子对中的每一个原子. 这种处理方法当然不尽合适. 因此,计算所得电荷分布的数值仍带有一定近似性. (3) 详细计算了 D_{2d} 对称构型丙二烯分子的分子轨道,结果见表 5. 计算中采用 35 个基函数,因此获得了 35 个分子轨道. 其中第 1 到第

第 11 轨道为填满轨道, 每个轨道填充两个电子, 且自旋相反. 从第 12 轨道以上为空轨道.

表 5 D_{2d} 对称丙二烯分子轨道

编号	对称性	E/J	电子数	编号	对称性	E/J	电子数
1	$1a_1$	$-4.900\ 619\ 04 \times 10^{-17}$	2	12	$3e$	$7.661\ 105\ 24 \times 10^{-19}$	0
2	$1b_2$	$-4.889\ 403\ 38 \times 10^{-17}$	2	13	$3e$	$7.661\ 105\ 24 \times 10^{-19}$	0
3	$2a_1$	$-4.889\ 346\ 05 \times 10^{-17}$	2	14	$4a_1$	$9.093\ 667\ 34 \times 10^{-19}$	0
4	$1b_1$	$-4.714\ 982\ 63 \times 10^{-18}$	2	15	$4b_2$	$1.008\ 668\ 81 \times 10^{-18}$	0
5	$2b_2$	$-4.199\ 300\ 07 \times 10^{-18}$	2	16	$4e$	$1.285\ 232\ 58 \times 10^{-18}$	0
6	$3a_1$	$-3.101\ 534\ 06 \times 10^{-18}$	2	17	$4e$	$1.285\ 232\ 58 \times 10^{-18}$	0
7	$3b_2$	$-2.754\ 422\ 84 \times 10^{-18}$	2	18	$5b_2$	$2.221\ 034\ 99 \times 10^{-18}$	0
8	$1e$	$-2.648\ 337\ 41 \times 10^{-18}$	2	19	$5a_1$	$2.251\ 774\ 56 \times 10^{-18}$	0
9	$1e$	$-2.648\ 337\ 41 \times 10^{-18}$	2	20	$6a_1$	$3.001\ 858\ 94 \times 10^{-18}$	0
10	$2e$	$-1.640\ 192\ 56 \times 10^{-18}$	2	21	$7a_1$	$3.453\ 025\ 67 \times 10^{-18}$	0
11	$2e$	$-1.640\ 192\ 56 \times 10^{-18}$	2	22	$5b_2$	$3.530\ 395\ 70 \times 10^{-18}$	0

3 结论

丙二烯分子两种不同对称性构型中, D_{2d} 对称构型比 D_{2h} 对称构型更稳定.

参 考 文 献

1 Ditchfield R, Hehre W J, Pople J A. Self-consistent molecular-orbital methods (IX) — An extended gaussian-type basis for molecular-orbital studies of organic molecules[J]. J. Chem. Phys., 1971, 2(54): 724 ~ 725

2 黄贻深, 吴季怀. 二氯二茂锆络合物的有效势从头计算[M]. 华侨大学学报(自然科学版), 2000, 21(2): 138 ~ 140

3 印永嘉. 大学化学手册[M]. 济南: 山东科学技术出版社, 1985. 1 022 ~ 1 023

Molecular Structure of Propadiene as Seen from
Ab Initio Calculation in Quantum Chemistry

Huang Yishen Wu Jihuai

(College of Mater. Sci. & Eng., Huaqiao Univ., 362011, Quanzhou)

Abstract Two different symmetric configurations in the electronic structure of propadiene molecule are calculated by adopting PSHONDO-SCF full electronic ab initio calculation. As indicated by computed results, it is more stable for prapadiene to adopt D_{2d} symmetric structure rather than D_{2h} symmetric structure. The electronic structure of propadiene molecule (D_{2d}): (1) total energy—— $-5.042\ 946\ 20\ \text{J}$, frontline orbit—— $\text{HOMO } E(2e) = -1.640\ 192\ 56 \times 10^{-18}\ \text{J}$, $\text{LUMO } E(3e) = 7.661\ 105\ 24 \times 10^{-19}\ \text{J}$; (2) bond order—— $0.381\ 4$ for C-H bonded directly, $0.677\ 11$ for C=C bonded directly; (3) charge distribution—— $-0.175\ 8$ for C (1), $-0.224\ 8$ for C(2) and C(3), $0.156\ 4$ for H.

Keywords calculation in Quantum chenistry, propadiene, full electronic ab initio calculation