converted to the sulfonate ester, either (entry 20). Despite of this limitation, the present method would be advantageous over the existing ones, because of the mild reaction conditions and high yields.

## Experimental

**Alcoholysis of amides by sodium nitrite-chlorotrimethylsilane.** To a stirred solution of an amide (10 mmol), sodium nitrite (1.4 g, 20 mmol) and benzyltriethylammonium chloride (0.22 g, 1 mmol) in 20 mL of methanol was added chlorotrimethylsilane (4.3 g, 40 mmol). After 7-12 hours of reflux, the crude reaction mixture was analyzed by TLC or GC. The reaction mixture was treated with water (50 mL) and the product was extracted with ether (20 mL) twice. The combined ether extract was dried over anhydrous magnesium sulfate. The filtrate was concentrated on a rotatory-evaporator. The residue was purified either by silica gel column chromatography or by distillation through a short path.

**Alcoholysis of amides by *t*-butyl nitrite-chlorotrimethylsilane.** To a stirred solution of *t*-butyl nitrite (1.1 g, 15 mmol), an amide (10 mmol) in 20 mL of methanol was added chlorotrimethylsilane (2.2 g, 20 mmol). After refluxing the mixture for 14 hours, the product was isolated and purified following the procedure described above.

**Acetylation of alcohols by acetamide in acetonitrile.** In a 50 mL flask were placed sodium nitrite (20 mmol), acetamide (10 mmol), and an alcohol (30% excess) and acetonitrile (20 mL). Chlorotrimethylsilane (20 mL) was added to the mixture. After 10-12 hours of reflux, the crude reaction mixture was filtered and concentrated. The residue was treated with water, and extracted with ether. The product was isolated and purified following the procedure described above.

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## References

1. (a) Challis, B. C.; Challis J. A. In *Comprehensive Organic Chemistry*; Sutherland, I. O. Ed., Pergamon Press, Oxford, 1979; Vol. 2, pp 957-1065. (b) Challis, B. C.; Challis, J. A. *The Chemistry of Amides*; Zabicky, J. Ed.; Interscience: London, 1970; pp 816-846.
2. Greendle, W. J.; Thorsett, E. D. *J. Org. Chem.* **1981**, *46*, 5351.
3. (a) Lovejoy, D. J.; Vesper, A. J. *J. Chem. Soc. A*, **1968**, 2325. (b) Kim, Y. H.; Kim, K.; Park, Y. J. *Tetrahedron Lett.* **1990**, *31*, 3893.
4. Spelber, N.; Papa, N.; Schwenk, E. *J. Amer. Chem. Soc.* **1948**, *70*, 3091.
5. Olah, G. A.; Olah, J. A. *J. Org. Chem.* **1965**, *30*, 2386.
6. Wade Jr. L. G.; Silvey, W. B. *Org. Prep. Proc. Int.* **1982**, *14*, 357.
7. Lee, J. G.; Kwak, K. H.; Hwang, J. P. *Tetrahedron Lett.* **1990**, *31*, 6677.
8. Lee, J. G.; Cha, H. T. *Tetrahedron Lett.* **1992**, *33*, 3167.
9. Acetamide/sodium nitrite/chlorotrimethylsilane in acetonitrile can be developed as a mild acetylating agent for many alcohols of subtle structures. 1,2-cyclohexane-dimethanol was converted into the corresponding diacetate in 95% yield.
10. (a) Weiss, R.; Wagner, K.-G.; Hertel, M. *Chem. Ber.* **1972**, *117*, 1965. (b) Weiss, R.; Wagner, K.-G. *Chem. Ber.* **1972**, *117*, 1973.
11. Alkyl nitrites were produced and isolated in high yields from the reaction of alcohols with sodium nitrite and chlorotrimethylsilane.

# *Ab initio* and Spectroscopic Studies of Bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene)

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The electronic structure of the cross conjugated polyenes has drawn a great deal of attention due to their central double bond distortion in the electronically excited and low-lying ionized doublet states.[1,2] Evidence of this structural behavior is supported by the spectroscopic observation that the spectral shape of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene) (I) in the fundamental state corresponds to that of biphenyl (II) in the first electronically excited state and vice versa.[3] This spectroscopic behavior is explained by the specific difference of their π-electron distribution.[3]

The molecular structure of I has been studied in the gas phase[4] and crystal[5] by the gas electron and X-ray diffraction methods, respectively. In the gas phase, molecule I was found to have a dihedral angle of 9.7° in nonplanar carbocyclic rings that is described by $C_6$-$C_1$-$C_2$=$C_3$.[4] In the crystal, however, the molecule was found to deviate from planarity to different extent such that the torsional angles about single bonds and double bonds vary by only 5.1° and 1.2°, respectively.[5] It is noted for comparison that the torsional angle of the bond between the two phenyl rings in II is about 42° in the gas phase. In the solid state, however, the biphenyl molecule is planar.[6~10] This can be taken as an indication that crystal packing forces are sufficiently large to favorably compensate the steric strain. All six-membered rings are slightly in boat conformations due to the interactions between the ortho hydrogen atoms across the central double bond.[5]

Here we report fluorescence excitation spectroscopic studies of I cooled in pulsed supersonic expansions of He in the ranges 307-345 nm and *ab initio* studies of the electronic

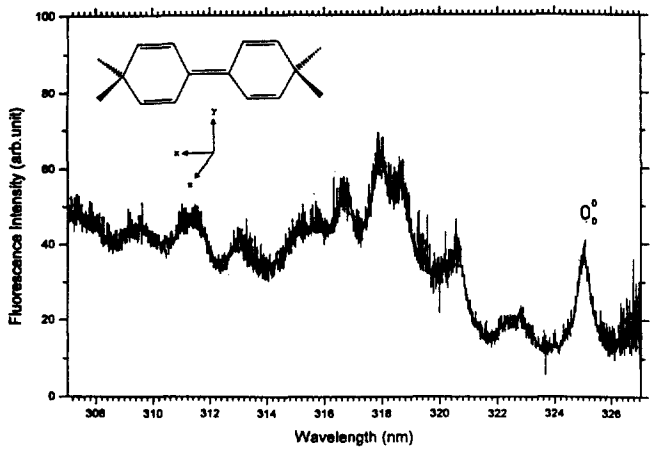


**Figure 1.** Fluorescence excitation spectrum of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene) in helium at $T_0=85$ ℃, where $T_0$ is the temperature of the fluorene sample in the nozzle.

structures and their energetics of the molecule.

## Experimental

Compound I was prepared by a reductive coupling of 4,4-dimethyl-2,5-cyclohexadienone (III) with $TiCl_3/LiAlH_4$.[11] Compound III was prepared from 4,4-dimethylcyclohexenone by an oxidation reaction using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[12]

A Newport pulse nozzle with a 0.5 mm slit was used for measuring the fluorescence excitation spectra of the molecule. Pressures of about $10^{-4}$ torr were achieved at stagnation pressures of 725 torr of He. A gaseous mixture of He seeded with I heated in the nozzle chamber to 85 ℃ was expanded through the nozzle. A Lambda Physik EMG MSC 104+FL3002 excimer-pumped dye laser (R6G) was used as an excitation source. The spectral resolution of the laser beam after doubling is 0.4 $cm^{-1}$. The laser pulse was synchronized with the electronic pulse to drive the nozzle. The laser beam crossed the supersonic free jet 15 mm downstream from the nozzle. The emission collected through a lens was detected with a Hamamatsu H 3177 photomultiplier.

The Standard *ab initio* calculations were carried out with the Cray YMP version of Gaussian 92.[13] The geometry was optimized by using the standard 3-21G[14] and 6-31G*[15] basis sets.

## Results and Discussion

The fluorescence excitation spectrum of the jet-cooled molecule I seeded in He is shown in Figure 1. The spectrum is shown only in the spectral range 307-327 nm since in the other spectral range 327-345 nm, any peak with reasonable intensity is not observed. The lowest energy spectral features of the isolated bare I molecule cooled adiabatically was observed at 30,760 $cm^{-1}$ (325.1 nm) with reasonable intensity. The spectral feature is tentatively assigned to the electronic origin of the lowest spin-allowed $S_0 \rightarrow S_1$ transition. Our quantum mechanical calculations using the standard 3-21G and 6-31G* basis sets indicates that the electronic transition to the lowest $S_1$ state is a $^1A_g \rightarrow {}^1B_{3u}$ transition in the $D_{2h}$ symmetry, with the electronic transition dipole moment being polarized along the long-axis ($x$-axis). Previously the $\lambda_{max}=319.0$ nm is reported to the $^1A_g \rightarrow {}^1B_{3u}$ electronic transition determined in the gas phase, the value being much higher in energy than our value determined by a free jet expansion method.

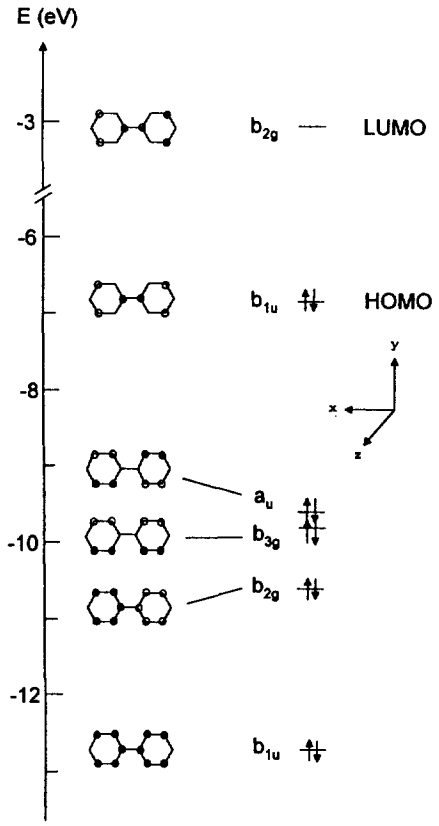


**Figure 2.** π-Molecular orbitals of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene) and their energetics derived by using the 6-31 G* basis sets.

The spectral broadness of the various electronic vibrational bands seen in Figure 1 may arise from the torsional rotation about the central double bond during the electronic excitation. The rotation about the double bond may give rise to enhance the number of the vibrational density of states in the electronic excited state resulting in the spectral broadening of the fluorescence excitation spectrum.

IR and Raman spectra are measured in the solid state to elucidate the conformation of I in the fundamental state.[16] It is found that the rule of mutual exclusion holds for the IR and Raman spectra, thus indicating that molecule I has a center of symmetry in the solid state.

The electronic structure of I was theoretically studied by the HF/3-21G and HF/6-31G* calculations. The MO energy levels and the orbital symmetries derived by the HF/6-31G* calculations are shown in Figure 2 and listed in Table 1.

The orbital energies determined from the higher level calculations using the 6-31G* are in better agreement with the photoelectron spectroscopic results. Note that the HOMO and LUMO gap in Figure 2 is determined experimentally from the 0-0 band observed in Figure 1. It is noted that the orbital

**Table 1.** Orbital energies (eV) of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene) based on calculation using the 3-21G and 6-31G* basis sets

| MO | Exptl.[a] | Calcd. | |
|---|---|---|---|
| | | 3-21G | 6-31G* |
| $b_{1u}$ | −7.05 | −6.851 | −6.868 |
| $a_u$ | −9.07 | −9.783 | −9.614 |
| $b_{3g}$ | −9.24 | −9.973 | −9.807 |
| $b_{2g}$ | −10.23 | −10.678 | −10.613 |
| $b_{1u}$ | − | −12.770 | −12.746 |

[a] Based on the photoelectron spectra of bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene), ref 2.

symmetries shown in Figure 2 are based on the $D_{2h}$ symmetry since the fully optimized structure of 1 has the $D_{2h}$ molecular symmetry. The theoretical values listed in Table 1 stand in accord with the measured ionization energies.

Why the molecule deviates from planarity more in the excited state than in the ground-state? As shown 2, the central C=C bond order is reduced in the electronically excited state due to the participation of the antibonding character of the bridged C=C bond in the LUMO with the $b_{2g}$ symmetry. Thus the deviation of the carbocyclic moieties from planarity may be facilitated such that the repulsion between the ortho hydrogen atoms across the central double bond is decreased.

In conclusion, we measured the fluorescence excitation spectrum of I cooled in supersonic free jets and calculated the π molecular orbitals and their energetics. The electronic excitation with lowest energy is determined as a spin-allowed $^1A_g \rightarrow {}^1B_{3u}$ transition. The MO calculation is quite informative as to the bond order and to estimates of orbital energies. Further assignments of the electronic vibrational bands in the fundamental and excited states are now performed.

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## References

1. (a) Bally, T.; Haselbach, E. *Helv. Chim. Acta* **1975**, *58*, 321. (b) Bally, T.; Buser, U.; Haselbach, E. *Helv. Chim. Acta* **1978**, *61*, 38.
2. Bally, T.; Neuhaus, L.; Nitsche, S.; Haselbach, E.; Janssen, J.; Lüttke, W. *Helv. Chim. Acta* **1983**, *66*, 1288.
3. Janssen, J.; Lüttke, W. *J. Mol. Struct.* **1882**, *81*, 207.
4. Traetteberg, M.; Bakken, P.; Almenningen, A.; Lüttke, W.; Janssen, J. *J. Mol. Struct.* **1982**, *81*, 87.
5. Noltemeyer, M.; Janssen, J.; Lüttke, W. *J. Mol. Struct.* **1982**, *81*, 105.
6. Robertson, G. M. *Nature (London)* **1961**, *191*, 593; **1961**, *192*, 1026.
7. Trotter, J. *Acta Crystallogr.* **1965**, *14*, 1135.
8. Hargreaves, A.; Rizvi, S. H. *Acta Crystallogr.* **1962**, *15*, 365.
9. Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1976**, *32*, 1420.
10. Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1976**, *33*, 1586.
11. Janssen, J.; Lüttke, W. *Chem. Ber.* **1982**, *115*, 1234.
12. Zimmermann, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653.
13. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1992.
14. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
15. Hehre, W. J.; Radom, L.; Schleyer, R. V. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
16. Infrared and Raman spectra of **I** were also measured in our laboratory. The spectral assignments are under way.