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Electronic Structures and Oxidation Potentials of Some Azulene Derivatives

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The electronic structures of azulene (**1**) and its alkylated derivatives were investigated on the basis of MO calculations by MNDO and PM3 method. There results were experimentally evaluated by measuring the oxidation potentials (E^{ox}) of **1** and its alkylated derivatives, from which the additive property on E^{ox} was suggested as shown by $E^{\text{ox}}(\text{Az.subst}) = E^{\text{ox}}(\text{AZ}) - 0.10n_{1,3} + 0.06n_2 - 0.02n_{4,8} - 0.11n_{5,7} - 0.01n_6$. Thus, the alkyl groups at the 1,3- and 5,7-positions lower the E^{ox} values by ca. 0.1 V, and stronger donating properties were observed for 3-methylguaiazulene ($E^{\text{ox}} = +0.53$ V) and 3,3′-biguaiazulene ($E^{\text{ox}} = +0.40$ V). The redox properties of guaiazulenyl sulfides which were prepared from guaiazulene via a phenylsulfonylthio derivative were also studied. Unlike the alkylated azulenes they underwent reversible one-electron oxidations and exhibited stronger donating properties ($E^{\text{ox}} = +0.40 - +0.44$).

Since the early stages of studies on azulene chemistry, it has been found that electrophilic reactions tend to occur at the 1,3-positions of the azulene nucleus, and also at the 5,7-positions for 1,3-disubstituted azulenes.[1—3] These reactions are governed by the MO coefficients of the HOMO, as suggested by the higher reactivity at the 2,4,6-positions for 2-amino- and 2-hydroxyazulenes.[4] On the other hand, one of the authors and his co-workers have recently found an intriguing characteristic of 3-bromoguaiazulene (**19**) obtained by the bromination of guaiazulene (**7**).[5] **19** was stable in hexane, but upon dissolution in benzene formed 3,3′-biguaiazulene (**18**) as well as side-chain brominated derivatives (**12** and **13**) and dehydrobrominated compound **14**. Compounds **12** and **13** easily derived to alcohols **15**—**17** at room temperature (Chart 1).[5a,5b] It is interesting to note that compound **19** in methanol produced bromine-free dimer **18**, trimers, and oligomers, together with a small portion of methoxylated products.[5b,5c] Such solvent-dependency is quite novel and the lability of 3-bromoguaiazulene (**19**) could be accounted for by the easy one-electron oxidation of the guaiazulene nucleus. In this connection, it is of interest to study the electronic structure and MOs of azulenes in terms of the effects of alkyl substituents on the donating properties of the azulene nucleus.

Experimental

Materials. Compounds **2**—**6** and **9**—**18** were prepared according to the literature method.[6]

Preparation of 3-(Phenylsulfonylthio)guaiazulene (23). To a solution of 1.60 g (5.10 mmol) of bis(phenylsulfonyl)sulfide[7] in dichloromethane (30 mL) was added a solution of guaiazulene (**7**) (1.01 g, 5.08 mmol) in 10 mL dichloromethane and 15 g of SiO_2. Evaporation of the solvent under reduced pressure gave **23** adsorbed on SiO_2. Elution with dichloromethane followed by recrystallization from acetone gave violet needles of **23** (1.63 g) in an 85% yield.

Mp 110—115 °C; IR (KBr) 1446, 1392, 1368, 1310, 1138, 1080, 595, and 535 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.39$ (6H, d, $J = 7$ Hz), 2.54 (3H, s), 2.89 (3H, s), 3.13 (1H, sep, $J = 7$ Hz), 7.14 (1H, d, $J = 11$ Hz), 7.25—7.51 (5H, m), 7.37 (1H, dd, $J = 1$ Hz, 11 Hz), 7.54 (1H, s), and 8.24 (1H, d, $J = 1$ Hz); MS *m/z* (rel intensity) 370 (M$^+$; 22) and 338 (100). Found: C, 66.69; H, 6.50%. Calcd for $C_{21}H_{22}O_2S_2\cdot 0.5H_2O$: C, 66.46; H, 6.11%.

Preparation of 3-Methylthioguaiazulene (20). To a solution of 3-(phenylsulfonylthio)guaiazulene (**23**) (200 mg, 0.54 mmol) in 10 mL dry THF was added dropwise 0.77 mL of MeLi (0.70 M in ether, 0.54 mmol, M = mol dm^{-3}) at −78 °C under nitrogen. After stirring for 80 min at this temperature, the mixture was poured into 30 mL of water and extracted with dichloromethane (40 mL×3). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. Evaporation of solvent followed by chromatographic separation on Al_2O_3 (hexane) afforded 26 mg of sulfide **20** in a 20% yield as light green crystals.

Mp 47—49 °C; IR (KBr) 2950, 1540, 1440, 1380, 1365, 1320, 1305, 920, 905, 835, 805, and 635 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.32$ (6H, d, $J = 7$ Hz), 2.50 (3H, s), 2.58 (3H, s), 2.97 (1H, sep, $J = 7$ Hz),

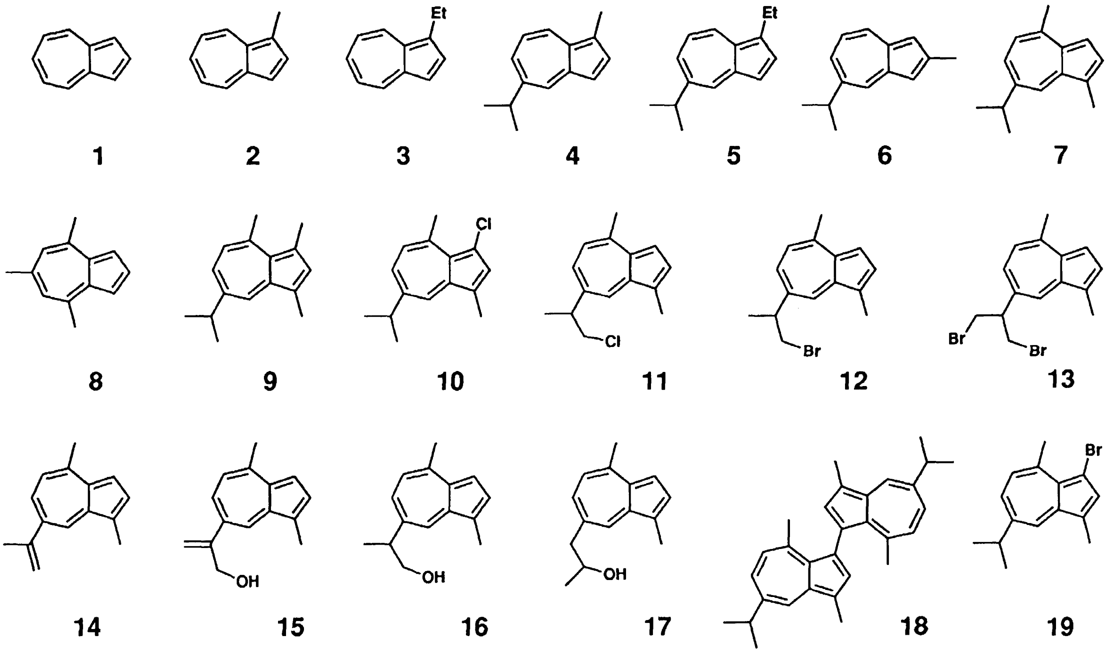


Chart 1.

3.18 (3H, s), 6.78 (1H, d, $J=11$ Hz), 7.22 (1H, dd, $J=2$ Hz, 11 Hz), 7.54 (1H, s,) and 7.97 (1H, d, $J=2$ Hz); MS *m*/*z* (rel intensity) 244 (M^+; 100) and 229 (70); UV (MeCN) λ_{max} (log ε) 648 (2.35), 390 (3.88), 374 (3.91), 360 (3.79 sh), 308 (4.42), 306 (4.41), 260 (4.31 sh), 250 (4.36), and 226 (4.25) nm. Found: C, 75.13; H, 8.29%. Calcd for $C_{16}H_{20}S \cdot 0.5H_2O$: C, 75.89; H, 8.30%.

Preparation of 3-Butylthioguaiazulene (21). To a solution of 3-(phenylsulfonylthio)guaiazulene (**23**) (200 mg, 0.54 mmol) in 10 mL dry THF was added dropwise 0.34 mL of *n*-BuLi (1.6 M in hexane, 0.54 mmol) at −78 °C under nitrogen. After stirring for 15 min at this temperature, the mixture was poured into 30 mL of water and extracted with dichloromethane (40 mL×3). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. Evaporation of solvent followed by chromatographic separation on Al_2O_3 (hexane) afforded 21 mg of sulfide **21** in a 14% yield as a deep blue tar.

IR (KBr) 2950, 1542, 1460, 1384, 1368, 1320, 1283, 1200, 1048, 915, 809, and 640 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta=0.90$ (3H, t, $J=7$ Hz), 1.32 (6H, d, $J=7$ Hz), 1.43 (2H, tq, $J=7$ Hz, 7 Hz), 1.61 (2H, tt, $J=7$ Hz, 7Hz), 2.59 (3H, s), 2.88 (2H, t, $J=7$ Hz), 2.98 (1H, sep, $J=7$ Hz), 3.22 (3H, s), 6.82 (1H, d, $J=11$ Hz), 7.28 (1H, dd, $J=2$ Hz, 11 Hz), 7.58 (1H, s), and 7.99 (1H, d, $J=2$ Hz); MS *m*/*z* 286 (M^+; 100); UV (MeCN) λ_{max} (log ε) 640 (2.61), 390 (3.73), 3.74 (3.86 sh), 362 (3.78), 308 (4.34), 294 (4.40 sh), 248 (4.32 sh), and 228 (4.21) nm. Found: C, 77.31; H, 9.24%. Calcd for $C_{19}H_{26}S \cdot 0.5H_2O$: C, 77.29; H, 9.15%.

Preparation of Di-3-guaiazulenyl Sulfide (22). To a solution of 3-(phenylsulfonylthio)guaiazulene (**23**) (95 mg, 0.30 mmol) and guaiazulene (**7**) (100 mg, 0.51 mmol) in 20 mL dichloromethane was added 10 g of SiO_2. The solvent was then evaporated under reduced pressure. The mixture was allowed to stand for 1 h and then eluted with dichloromethane. The resulting green tar was chromatographed on Al_2O_3 (hexane; hexane/ether = 100/1 as eluents), affording 27 mg of **22** in a 25% yield as deep green rods. Starting materials (**23**: 14 mg, 7% and **7**: 19 mg, 19%) were also recovered upon chromatography.

Mp 175—176 °C; IR (KBr) 2995, 1543, 1446, 1384, 1367, 1321, 1282, 1160, 1115, 920, 815, and 640 cm^{-1}; ^1HNMR ($CDCl_3$) $\delta=1.33$ (6H, d, $J=7$ Hz), 2.49 (3H, s), 2.98 (1H, sep, $J=7$ Hz), 3.19 (3H, s), 6.81 (1H, d, $J=11$ Hz), 7.20 (1H, s), 7.24 (1H, dd, $J=2$ Hz, 11 Hz), and 7.98 (1H, d, $J=2$ Hz); MS *m*/*z* (rel intensity) 426 (M^+; 49), 198 (100), 183 (98), 165 (54), and 153 (50); UV (MeCN) λ_{max} (log ε) 622 (3.05), 392 (4.29), 378 (4.26), 320 (4.59 sh), 310 (4.65), 294 (4.71), 248 (4.61), and 232 (4.67 sh) nm. Found: C, 84.20; H, 8.20; S, 7.35%. Calcd for $C_{30}H_{34}S$: C, 84.45; H, 8.03; S, 7.51%.

Computational Methods. Calculations were carried out using a MOPAC package and using MNDO and PM3 approaches.[8] MO calculations were performed on a FACOM M770 computer at the Josai University Information Sciences Research Center.

Electrochemical Measurements. Oxidation potentials of azulene derivatives were measured by cyclic voltametry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte. All values shown in the text and tables are in *E*/V vs. SCE, and were measured under the same conditions by using Pt wire as a working electrode. In the case of irreversible waves (E_1^{ox} of **1**—**17** and E_2^{ox} of **21**—**22**), the half-wave potentials were estimated from the anodic peak potentials (E^{pa}) as $E^{ox}=E^{pa}-0.03$.

X-Ray Structural Analysis of Di-3-guaiazulenyl Sulfide (22). A green cube-like crystal with dimensions of 0.3×0.3×0.25 mm was obtained upon recrystallization of **22** from hexane. Intensity data collection was performed on an Enraf–Nonius CAD4 diffractometer by using Cu*Kα* (40 kV, 32 mA) radiation. A total of 3916 reflections was collected within $2\theta=130°$ at 23 °C. Crystal data are as follows: orthorhombic, $Pca2_1$ (No. 29), $a=30.088(4)$, $b=9.853(2)$, $c=17.207(2)$ Å, $V=5101(1)$ Å^3, $Z=8$, $D_c=1.110$ g cm^{-3}, $\mu_{Cu\,K\alpha}=11.720$ cm^{-1}. The structure was solved by the direct method by using the RANTAN81 program[9] with some modification and refined by the block-diagonal least-squares method. Anisotropic temperature factors were applied, and hydrogen atoms were not included in the refinement. The final *R* value was 8.42% for 3077 reflections with $|F_o|>3\sigma|F_o|$ and 560 parameters.

There are two crystallographically independent molecules (A and B) of **22** in the crystal. Their molecular geometries are very close to each other. Relatively large estimated standard deviations for the bond lengths (0.010—0.030 Å) and the angles (0.4°—1.9°) prevented detailed comparisons of these values between molecules A and B as well as between two guaiazulenyl moieties in the same molecule.

Results and Discussion

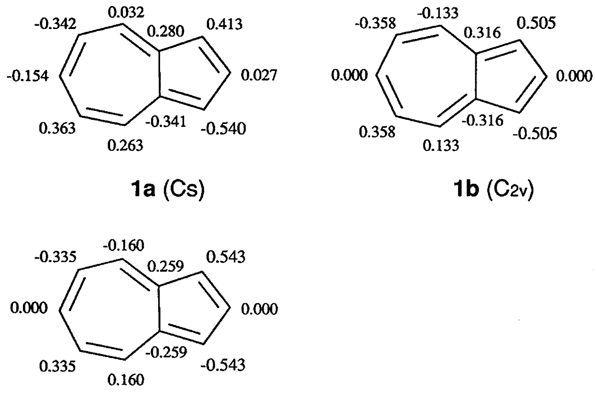
There have been several reports on the electronic structure of azulene (**1**) from experimental and theoretical points of view. On the basis of X-ray structural analysis, Robertson and co-workers concluded that the molecular symmetry of **1** is Cs,[10] which was supported by Hanson who determined the X-ray structure of the molecular complex of **1** with trinitrobenzene.[11] On the other hand, the geometrical structure of gaseous **1** is still ambiguous, but was suggested to be C_{2v}-symmetry according to electron diffraction studies. The diamagnetic ring current of the azulene nucleus results in the appearance of ^{1}H NMR chemical shifts in the range of 6.92—8.12 ppm, and only 6 signals in the ^{13}C NMR spectrum indicate the C_{2v} symmetry of **1** in solution.[12,13] The normal vibrations in the IR and Raman spectra were also analyzed by supposing the C_{2v} structure for **1**.[14] Besides the experimental studies of **1**, the dipole moment, the electronic spectrum, and the chemical reactivity and stability were first subjected to a theoretical study in comparison with naphthalene by means of HMO and PPP methods.[15] Later, theoretical approaches were conducted by using semi-empirical and ab initio methods,[16] yet the true molecular symmetry of **1** has been the subject of controversy. Herein we have reinvestigated the electronic structure of **1** by MNDO and PM3 methods.[8]

Azulene **1** has a permanent dipole moment of 1.0 D.[17] The present MNDO and PM3 calculations gave dipole moments for **1** in C_s symmetry of 1.01 and 1.87 D, respectively, and in C_{2v} symmetry of 1.60 and 1.86 D, respectively. Thus, the azulene skeleton is predicted to have C_s symmetry with rapid conversion between two structures of lower symmetry at the PM3 level calculation. The values of the heat of formation of **1a** and **1b** are calculated to be 81.378 and 82.309 k cal mol^{-1}, respectively. The magnitudes of the π-HOMO coefficients for **1a** is in the order of C-1 (−0.540) > C-3 (0.413), while for **1b** is in the order of C-1 (0.505) > C-5 (−0.358) (Fig. 1). Thus, the magnitude of the π-HOMO coefficients at the C-8 position of the heptafulvene moiety in the azulene molecule is larger than those of other positions.

In Table 1 are shown the calculated energy levels of the HOMO by means of the PM3 method as well as the oxidation potentials (E^{ox}) determined by cyclic voltammetry (CV). Azulene (**1**) underwent one-electron oxidation at +0.88 V, which is pretty low as a condensed aromatic hydrocarbon. Alkyl substituents strengthen the donating properties of the azulene nucleus. Especially introduction to the 1,3- and 5, 7-positions lowers the E^{ox} value by ca. 0.1 V. These results are agreement with the large MO coefficients of the HOMO at the 1,3,5,7-positions calculated by HMO and/or PM3 (C_{2v} symmetry) methods. On the other hand, alkyl groups at the 4,8-positions are less effective due to the small coefficients of these in the HOMO. The CV study of **1**—**9** suggested the additive property of alkyl groups on E^{ox} as shown by Eq. 1:

$$E^{ox}(\text{Az.subst}) = E^{ox}(\text{AZ}) - 0.10n_{1,3} + 0.06n_2 - 0.02n_{4,8} - 0.11n_{5,7} - 0.01n_6 \qquad (1)$$

n indicates the number of alkyl groups and the subscript represents the represents the position of the substituent. This equation has some uncertainty due to the small number of compounds used for its derivation, and the effects of an alkyl group at the 2-position are also inconsistant on the basis of the perturbation theory. Nevertheless, it seems useful for estimating the E^{ox} values of alkylated azulenes qualitatively, and the value for the unknown 3-methyl-5-isopropylguaiazulene is expected to be as low as +0.42 V. Functionalization at the side chain of guaiazulene (**7**) induced the expected perturbation on the oxidation potentials of the azulene nucleus. Thus, halogenation of the isopropyl group in **11**—**13** weakened the donating properties because the haloalkyl group no longer works as a donating group. Absence of the hyperconjugation effect in the isopropenyl group in **14**, **15** resulted in a slight increase of E^{ox} compared with **7**. A hydroxy group at the *β*-position of the alkyl group does not affect the oxidation potentials as can be seen in **16**, **17**.



1a (Cs)

1b (C2v)

HMO

Fig. 1. π-HOMO coefficients of azulene (**1**) by PM3 method.

Among the alkylated azulenes, 3,3′-biguaiazulene (**18**) is of special interest because it undergoes reversible two-stage one-electron oxidations (Fig. 2). Such redox behavior corresponds to its molecular framework, namely the vinylogue of heptafulvalene. In terms of the rotation of the molecular halves around the C3–C3′ bond, two geometries are

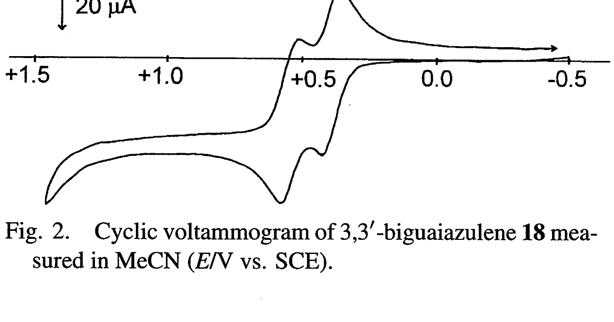


Fig. 2. Cyclic voltammogram of 3,3′-biguaiazulene **18** measured in MeCN (*E*/V vs. SCE).

Table 1. Oxidation Potentials[a] and Energy Levels[b]

Compd	E^{ox} (V)	HOMO (eV)	Compd	E^{ox} (V)	HOMO (eV)
1	+0.88	−8.161	**10**	+0.71	−7.856
2	+0.78	−8.048	**11**	+0.73	−7.952
3	+0.79	−7.982	**12**	+0.72	−7.978
4	+0.67	−7.925	**13**	+0.77	−8.051
5	+0.68	−7.914	**14**	+0.70	−7.921
6	+0.83	−8.080	**15**	+0.71	−8.072
7	+0.65	−7.891	**16**	+0.66	−8.049
8	+0.83	−7.996	**17**	+0.67	−7.882
9	+0.53	−7.789	**18**	+0.40	−7.336

a) E/V vs. SCE, all the voltammograms except **18** showed irreversible waves. Values of E^{ox} wave estimates as $E^{ox} = E_p - 0.03$ V. b) Energy levels were calculated by PM3 method.

expected for both the cation radical and the dication species (Scheme 1). Planar geometry seems advantageous for the delocalization of the charge and spin over the molecule yet steric interactions are present between the two methyl groups at the 4 and 4′ positions. In the twisted geometry, such repulsive interaction is now absent, and the two guaiazulene units are expected to behave independently upon electrochemical oxidation. The latter is not the case for **18** as seen by its two discrete oxidation potentials at +0.40 and +0.54 V. This idea is also supported by the calculation of the geometry optimized by the PM3 method (Fig. 3). Thus, planar geometry with a distance of 1.470 Å for the C3–C3′ bond was suggested to be the global minimum in spite of the short contact (1.66 Å) between the hydrogen atoms of the methyl groups. The twisted conformation is the geometry at the local minimum, whose energy is higher by 32.3 kcal mol^{-1} than the planar one. The HOMO of **18** is π-type with the lowest energy (−7.336 eV) among the azulenes examined here. The optimized geometries for $\mathbf{18}^{+\bullet}$ and $\mathbf{18}^{2+}$ are also planar, and the changes in bond lengths are in accord with the assumption that **18** behaves as a heptafulvalene vinylogue.

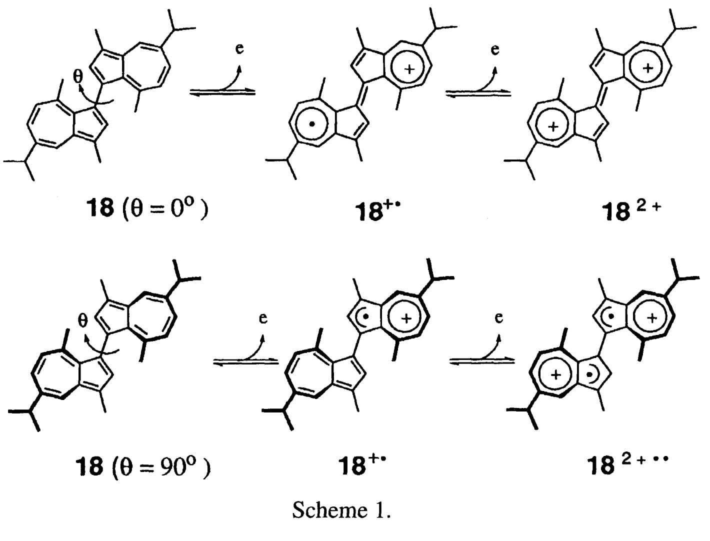
The above-mentioned studies on the alkylated azulenes indicate that the guaiazulenyl moiety is an intriguing building block in constructing novel multistage redox systems.[18] Protection of the labile 3-position by the proper substituent promises reversible redox behavior, although a methyl group is not sufficient for this purpose as shown by the irreversible wave in the voltammogram of **9**. Sulfur substituents seem suitable in this study considering their stabilization effects of the positively charged species. Starting from guaiazulene (**7**), three sulfides (**20**—**22**) were prepared by using phenylsulfonylthio derivative (**23**) as a common synthetic intermediate (Chart 2). Cyclic voltmmetry revealed that the alkylthio derivatives **20** and **21** underwent reversible one-electron oxidations as expected, and the value of E_1^{ox} are much lower than the simple alkylated azulenes (Table 2). In the case of di-3-guaiazulenyl sulfide (**22**), the second oxidation step is also reversible as in the case of 3,3′-biguaiazulene (**18**).

X-Ray structural analysis of **22** revealed that the two guaiazulenyl moieties are quite different from each other (Fig. 4).[19] Thus, one (Gu-1 group) is nearly coplanar with the C–S–C plane whereas the other (Gu-2 group) is almost

Table 2. Oxidation Potentials

Compd	E_1^{ox} (V)	E_2^{ox} (V)
20	+0.44	+1.01[a]
21	+0.44	+1.06[a]
22	+0.40	+0.71

a) Irreversible waves.



Scheme 1.

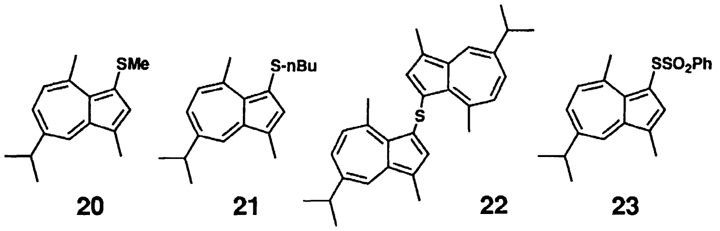


Chart 2.

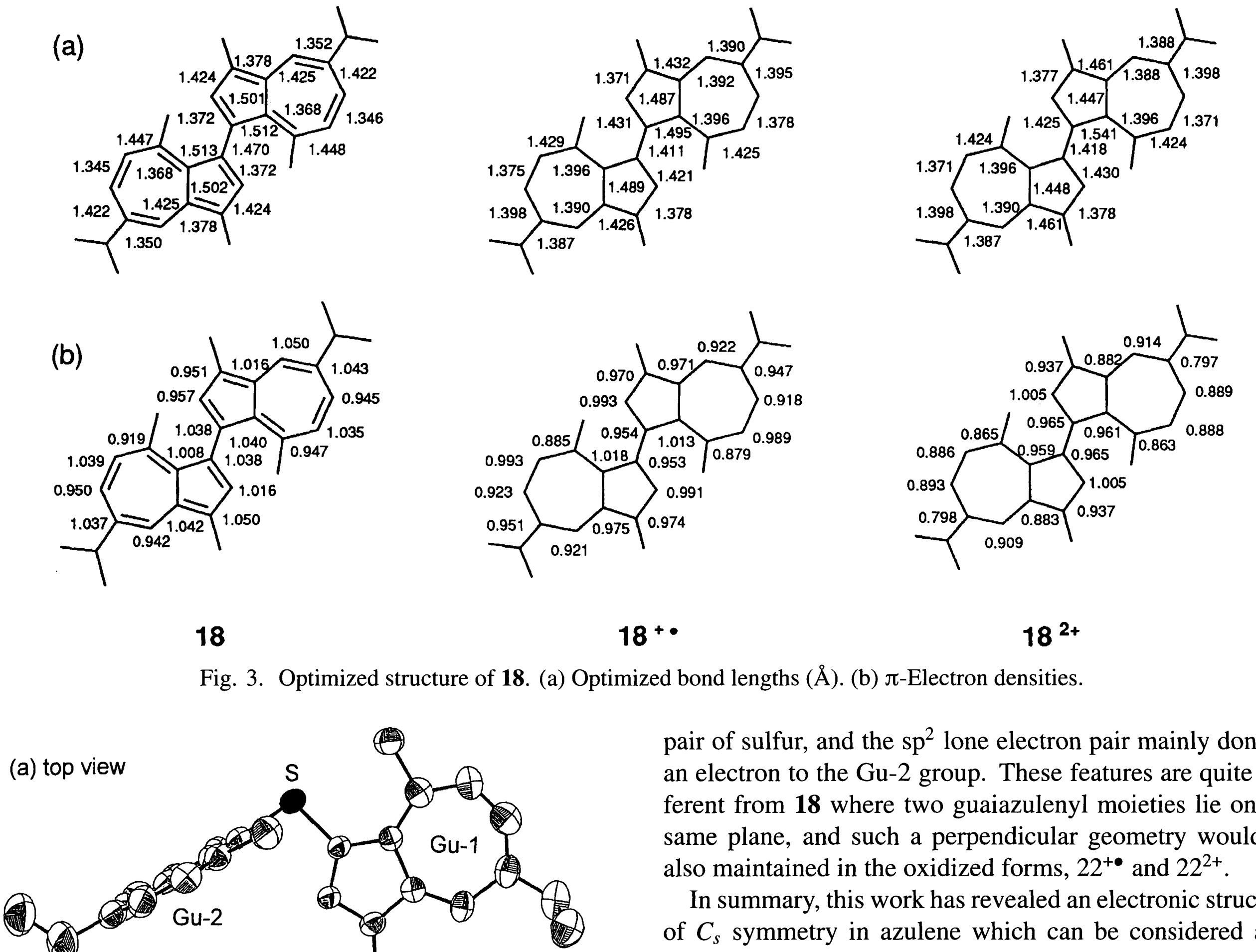


Fig. 3. Optimized structure of **18**. (a) Optimized bond lengths (Å). (b) π-Electron densities.

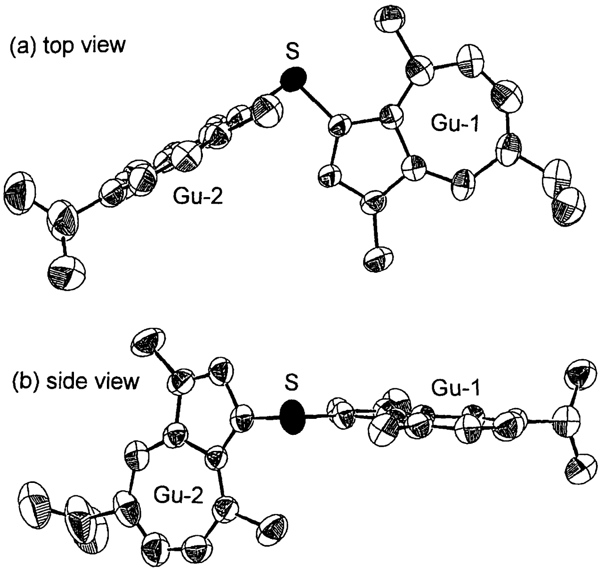


Fig. 4. (a) Thermal ellipsoids of **22** viewed perpendicularly to the C–S–C plane (one of the two crystallographically independent molecules). (b) The side view results from a 90 ° rotation around the horizontal axis.

perpendicular to that plane. These structural features indicate that the Gu-1 group conjugates with the 3p lone electron pair of sulfur, and the sp^2 lone electron pair mainly donates an electron to the Gu-2 group. These features are quite different from **18** where two guaiazulenyl moieties lie on the same plane, and such a perpendicular geometry would be also maintained in the oxidized forms, $22^{+\bullet}$ and 22^{2+}.

In summary, this work has revealed an electronic structure of C_s symmetry in azulene which can be considered as a heptafulvene vinylogue. In agreement with the MO calculations, the alkyl groups are very effective in increasing the donating properties of the azulene nucleus when introduced at the 1,3,5,7-positions. From these studies, the guaiazulenyl moiety is suggested to be an interesting building block in constructing reversible multistage redox systems. This idea was experimentally confirmed by investigating the redox properties of 3,3′-biguaiazulene (**18**) and 3-guaiazulenyl sulfides (**20**—**22**).

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