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Synthesis, molecular structure, and chemical reactivity of azuleno[1,2-*a*]acenaphthylene

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Abstract—The azuleno[1,2-*a*]acenaphthylene (**1a**) was prepared from 1-pyrrolidinylacenaphthylene (**5**) and 2*H*-cyclohepta[*b*]furan-2-one (**6**) by the method of the Takase–Yasunami azulene synthesis. Its ^{1}H and ^{13}C NMR spectra indicate that **1a** comprises azulene and naphthalene rather than acenaphtylene and heptafulvene in accordance with speculation drawn from a previous study of the DEPE calculations. The solid-state structure of **1a** was elucidated by X-ray crystallographical analysis, indicating that **1a** is nearly planar and exhibits little bond alternation as seen in the optimized structure at the MB3LYP/6-311G* level of theory. All bond lengths observed by the X-ray analysis are in good agreement within 0.024 Å with those calculated. Under pyrolytic conditions **1a** underwent azulene–naphthalene rearrangement to give **9** and **10**. The electrophilic substitution of **1a** was observed at the 7-position and the second reaction at the 3-position. The cycloaddition reaction of **1a** with dimethyl acetylenedicarboxylate (DMAD) yielded the 1:1 cycloadduct with a heptalene skeleton **16a** and the 1:2 cycloadduct **19**, along with the substitution product **17**. The X-ray structural analysis of the cycloadducts **16a** and **19** is also described.

1. Introduction

Fusion of azulene at the 1,2-positions of acenaphthylene produces three 1,2-*a*, 4,5-*a*, and 5,6-*a* isomers, **1a**[1], **2**[2], and **3**. Among them, the tetrasubstituted derivative of 1,2-*a* isomer **1b**[3], and the non-substituted 4,5-*a* isomer **2** have been synthesized. Also, two aza-derivatives of 1,2-*a* and 5,6-*a* isomers, acenaphtho[1,2-*b*]cyclohepta[*d*]pyrrole[4] and acenaphtho[1,2-*b*]cyclohepta[*e*]azepine[5], have appeared in the literature. The 1,2-*a* isomer **1a** can be recognized by two ways of fusion of two segments of hydrocarbons, i.e. it consists either of azulene and naphthalene or of hepta fulvene and acenaphthylene, shown by two broken lines in Figure 1. DEPEs (Delocalization Energy per π-electron) are previously calculated to be 0.023 for azulene, 0.055 for naphthalene, −0.002 for heptafulvene, and 0.039 for acanaphthylene,[6] suggesting that the contribution of the composition of azulene and naphthalene is preferred for **1a**. In order to clarify structural details of the 1,2-*a* isomer by X-ray crystallographical analysis and also its chemical behavior, we achieved a short-step synthesis of the non-substituted hydrocarbon **1a**. Herein we wish to give a full account of the synthesis, the X-ray analysis, and some reactions of **1a**.

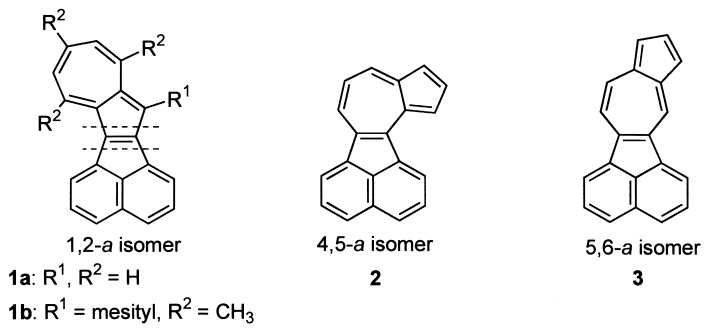

Figure 1.

Keywords: azuleno[12-*a*]acenaphthylene; delocalization; X-Ray; electrophilic substitution; cycloaddition.

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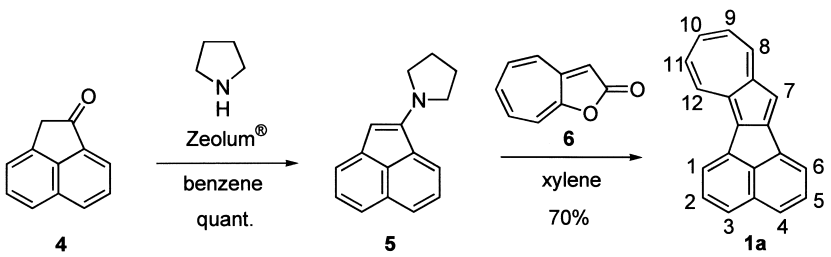


Scheme 1. Synthesis of **1a**.

2. Results and discussions

2.1. Synthesis

Takase and Yasunami developed a useful method for synthesizing azulenes from enamines and 2*H*-cyclohepta[*b*]furan-2-ones.[7] We accomplished the synthesis of **1a** from **5** according to their method. Although the enamine **5** was previously prepared by the reaction of acenaphthen-1-one (**4**) with pyrrolidine in refluxing benzene in high yield, it required a long reaction time and distillation for isolation.[8] We found that **5** can be prepared more conveniently using Zeolum® as a solid catalyst. After the mixture was stirred at room temperature for 12 h, filtration to remove the solid catalyst and evaporation of the filtrate gave a quantitative yield of enamine **5**. The reaction of **5** with 2*H*-cyclohepta[*b*]furan-2-one (**6**) in xylene at reflux for 4 h gave **1a** as dark green needles in 70% yield (Scheme 1). The crystals of **1a** are very stable and can be stored at room temperature for at least a year without any change. However, a solution of **1a** in halogenated solvents showed gradual decomposition.

2.2. Spectroscopic properties

The ^{1}H- and ^{13}C NMR spectra of **1a** in $CDCl_3$ show 12 proton signals and 20 carbon signals sufficient for the structure of **1a**. These signals were completely assigned based on the H–H COSY, HMQC, HMBC, and NOEDF spectra. The results are shown in Figures 2 and 3. Especially, NOE enhancement (7.5%) between H-1 and H-12, and correlation of the C-3b with any hydrogen in the HMBC spectrum were important for the assignment. All proton signals appear in the aromatic region between 7.05 and 8.50 ppm. The average of chemical shifts of all ring protons of **1a** is δ_{7-12} 7.61 ppm for the azulene moiety and δ_{1-6} 7.70 ppm for the naphthalene moiety. These values are nearly equal to those of the parent azulene (av. 7.61 ppm) and naphthalene (av. 7.63 ppm), respectively. The difference in $^{3}J_{H-H}$ coupling constants of the azulenyl protons is small (less than 0.7 Hz), indicating the less bond alternation in the azulene moiety compared with that of benz[*a*]azulene (maximum 2.9 Hz)[9] which exhibits clear bond alternation.

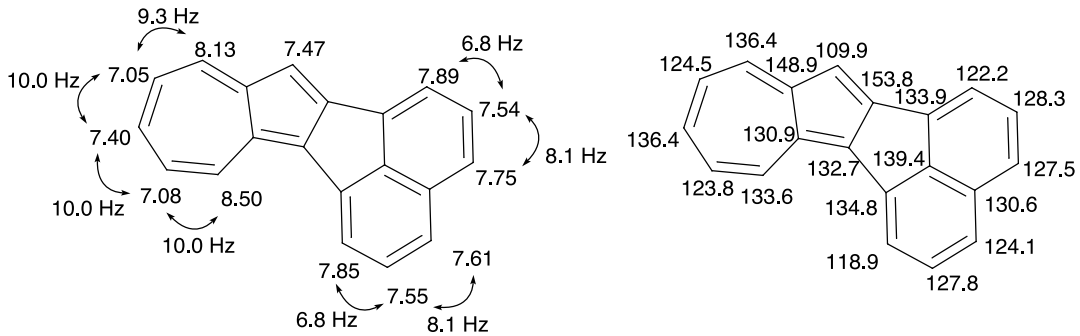


Figure 2. The assigned proton and carbon chemical shifts and coupling constants of **1a**.

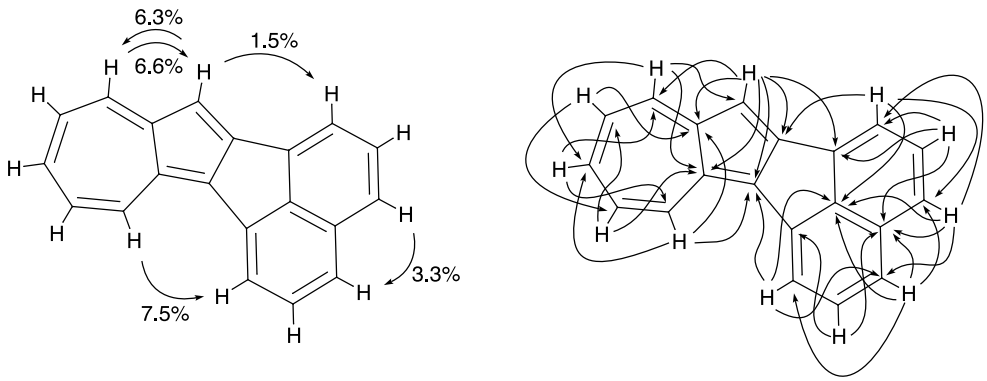


Figure 3. Correlation in the NOEDF (left) and HMBC (right) spectra of **1a**.

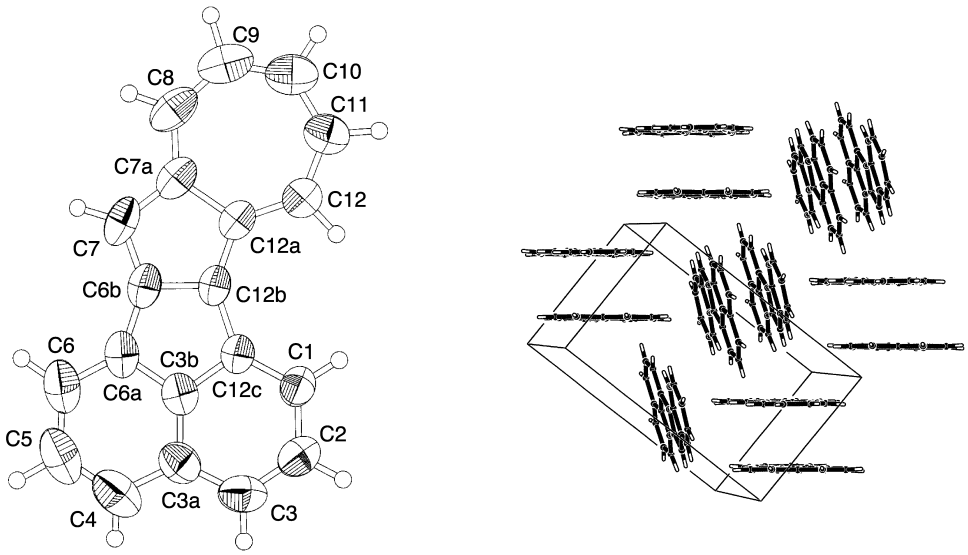


Figure 4. ORTEP drawing and perspective view of the packing of **1a**.

2.3. The X-ray crystallographical analysis and computational studies

The solid-state structure of **1a** was further elucidated by X-ray crystallographical analysis. Suitable green monoclinic crystals of **1a** for the analysis were obtained by recrystallization from a mixture of hexane and dichloromethane. The ORTEP drawing and perspecive view of packing of **1a** are shown in Figure 4. It showed that the molecule is nearly planar and maximum distance of the carbon atoms from the mean plane is 0.066 Å at the C-4 carbon atom (Fig. 5). In a unit cell four molecules of **1a** exist. They are piled in such a way that the dipole of the azulene moiety of the molecule rules out each other. The minimum non-bonded atomic distance is 3.427 Å between the C-9 atom and the C-12c atom of another molecule. The difference in the bond lengths of the seven-membered ring is very small, suggesting that there is little bond alternation in the azulene moiety. Also, the bond lengths of the azulene and naphthalene moieties of **1a** are nearly equal to those of the parent azulene,[10]and naphthalene,[11] respectively. Furthermore, the C6a–C6b and C12b–C12c bonds are 1.457 and 1.463 Å long, respectively, which are longer than of all other C–C bonds. Thus, it is also indicated that **1a** consists of azulene and naphthalene. The Tables of fractional atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. 12 Union Road, Cambridge CB2 1EZ, United Kingdom (CCDC 189847). The optimized structure of **1a** was obtained by calculations at the MB3LYP/6-311G* level of theory. This structure shows complete planarity and the bond lengths are slightly longer than those of the X-ray structure except the C3a–C4, C3b–C6a, C7a–C8 and C12b–C12c bonds (Fig. 6). It is noteworthy that the bond lengths are in good agreement with those of the structure revealed by X-ray crystallographical analysis. Although the largest difference between them (0.024 Å) is for the C9–C10 bond observed at the molecular edge, other differences are less than 0.016 Å.

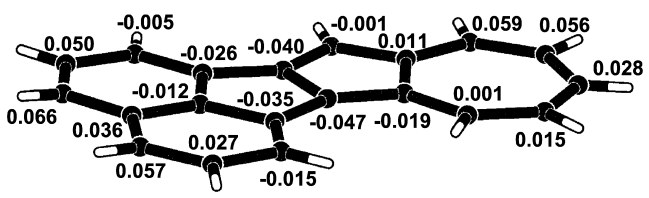


Figure 5. Distances (Å) of the carbon atoms from the mean right plane of **1a**.

2.4. Thermal rearrangement

The thermal rearrangement of azulene to naphthalene under thermolytic conditions has been well studied and is usually observed at 300–400°C.[12] Flash thermolysis of **1a** under nitrogen stream below 400°C gave a quantitative recovery and the reaction at 600°C provided a mixture of benz[*j*]-fluoranthene (**9**) (28%) and benz[*k*]fluoranthene (**10**) (14%), accompanied with a 58% recovery of **1a**. The transformation from **1a** into **9** and **10** probably proceeds via the norcaradiene forms **7a** and **7b**, as claimed by Wentrup[13] (Scheme 2). Reluctance to the rearrangement of **1a** compared with azulenes may be probably attributed to the acenaphthyl annulation which relatively stabilizes the azulene moiety mainly by electronic effect and destabilizes their norcaradiene valence isomers by increasing the angular strain much more in **7** than in the corresponding isomer of azulene itself.

2.5. The electrophilic substitution

The reaction of **1a** with bromine in the presence of triethylamine in dichloromethane exclusively gave the 7-bromo derivative **11** as green needles in 96% yield (Scheme 3). On the other hand, the reaction of **1a** with triethyl orthoformate in the presence of boron trifluoride diethyl etherate[14] also gave the 7-substituted product **13** as green needles in 84% yield. When the reaction was carried out by the typical Vilsmeier method using dimethyformamide (DMF) and phosphorus oxychroride ($POCl_3$), **13** was obtained in only 3% yield accompanied with a considerable

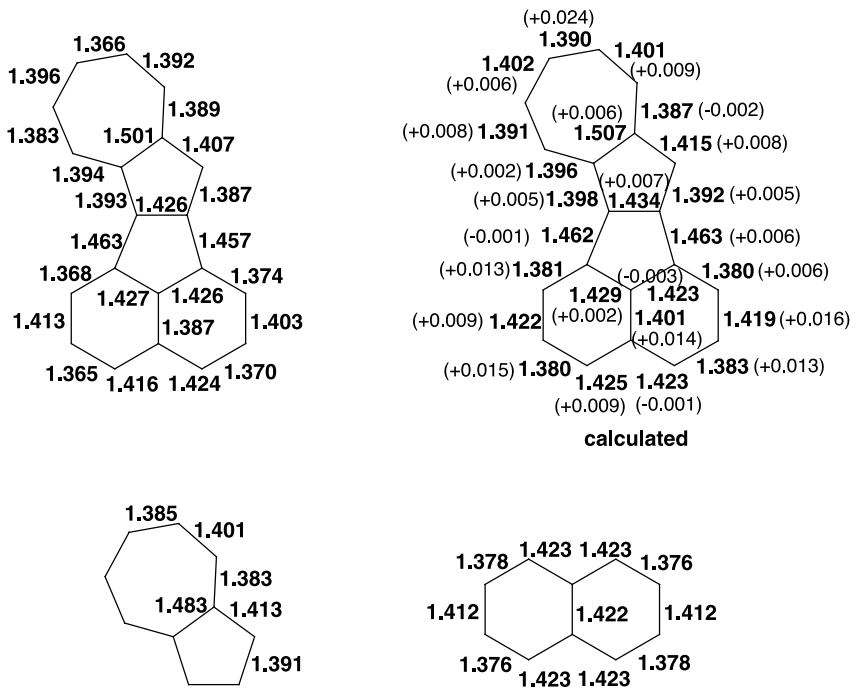
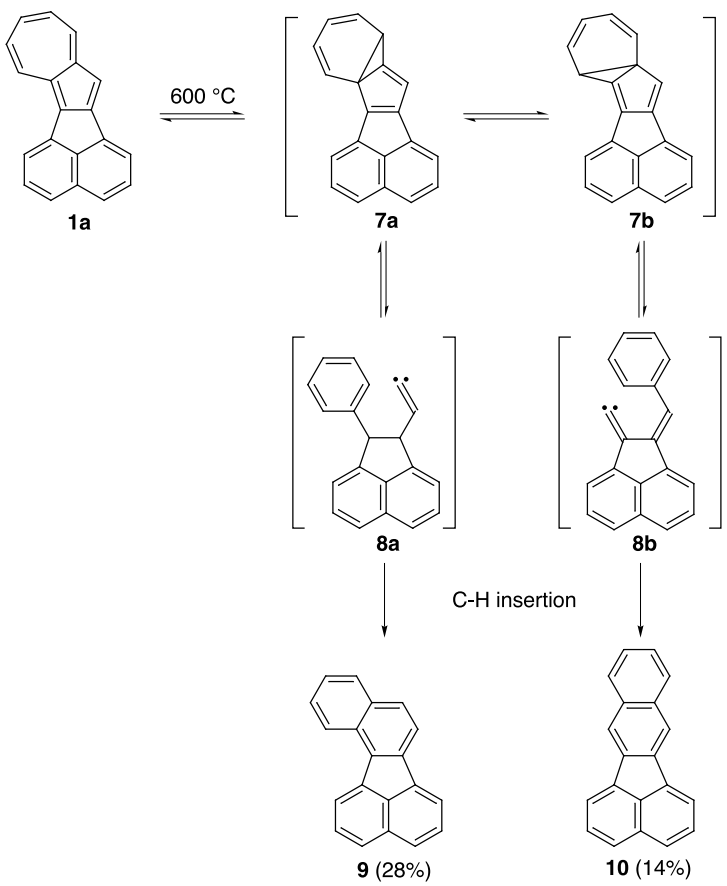
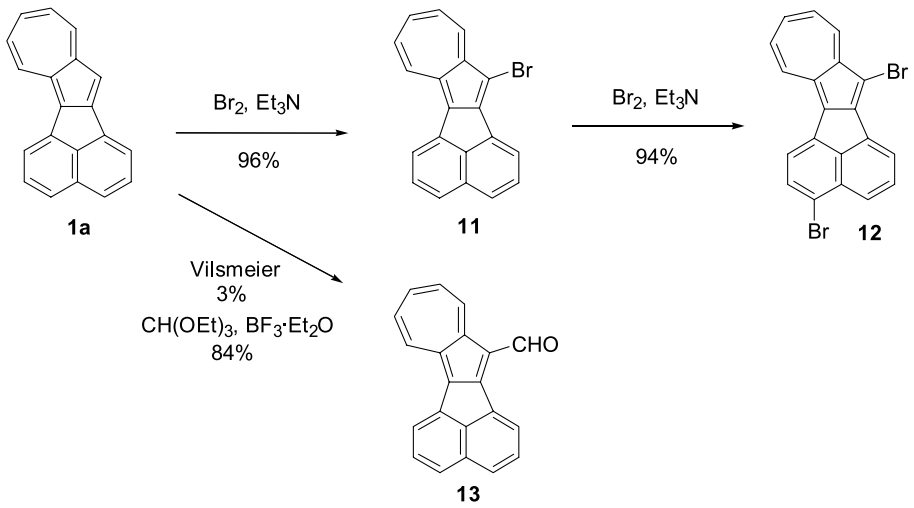


Figure 6. C–C bond distances (Å) of **1a**, azulene and napthalene by X-ray crystallographical analysis, and **1a** optimized by the MB3LYP/6-311G* calculations. Parenthesis are difference between the crystal and calculated structures.



Scheme 2. The thermal rearrangement of **1a**.



Scheme 3. The electrophilic substitution of **1a**.

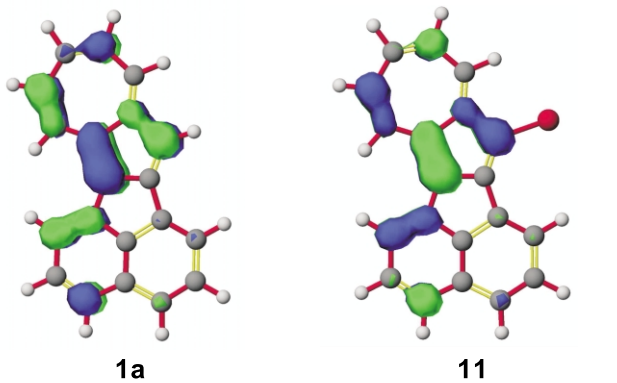


Figure 7. Molecular orbital drawings of the HOMOs of **1a** and **11** calculated by the PM3 method.

amount of an unidentified complex mixture. The high reactivity at the 7-position of **1a** can be explained by the highest coefficient at this position except the quaternary carbons in its HOMO calculated by the PM3 method as we have already discussed in the protonation of **1a**.[15] Furthermore, we found that bromination of **11** occurred exclusively at the 3-position to give 3,7-dibromo derivative **12** in 94% yield (Fig. 7). While the coefficients at 1-, 3-, and 11-positions in the HOMO of **11** are nearly equal, calculated heats of formation of the protonated species predict that the **11H$^+$c** is the most stable intermediate among them (Fig. 8). The structures of **11**–**13** were confirmed by the spectral and analytical data. The ring protons of **1a**, **11** and **12** were observed in the region of 7.62–8.51 ppm, while those of the 7-fomyl derivative **13** resonate at slightly lower field. The average (8.23 ppm) of the ring proton shifts of **13** is ca. 0.5 ppm more than those of the others. Their UV–vis spectra of **1a**, **2**, **11** and **13** are shown in Chart 1. These spectra exhibit three similar main bands except for 7-formyl derivative **13** whose longest absorption (878 nm) shows a bathochromic shift by ca. 70–100 nm. The longer absorption maximum and the low field shift of the ring proton of **13** compared to those of others can be attributed to the effect of the strong electron-withdrawing nature of a formyl group.

The electrophilic substitution of **1a** revealed greater reactivity at the azulene moiety than at the naphthalene moiety, and that the reaction position of each moiety is the same as that observed usually in azulene or naphthalene itself; it is as if two independent molecules of azulene and naphthalene themselves existed in the molecule of **1a**.

2.6. Cycloaddition reaction

Hafner first reported that the periselective cycloaddition reactions of the azulenes with dimethyl acethylene-dicarboxylate (DMAD) gave the heptalene derivatives.[16] Later, Hansen studied the reaction in polar media and in the presence of a Lewis acid catalyst.[17] As shown in the electrophilic reaction, we can expect that cycloaddition of **1a** will proceed at the azulene part. Indeed, the reaction of **1a** with DMAD in refluxing xylene gave the 1:1 cycloadduct **16a**, the 1:2 cycloadduct **19** with two molecules of DMAD

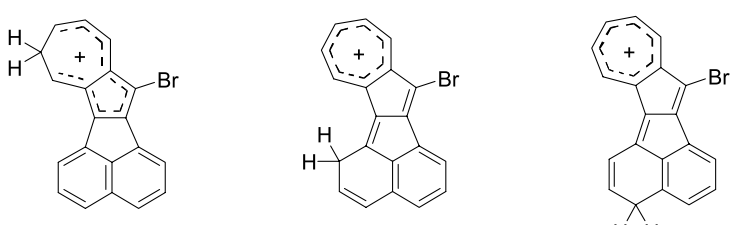


Figure 8. The heats of formation of **11H$^+$a**, **11H$^+$b**, and **11H$^+$c** calculated by the PM3 method.

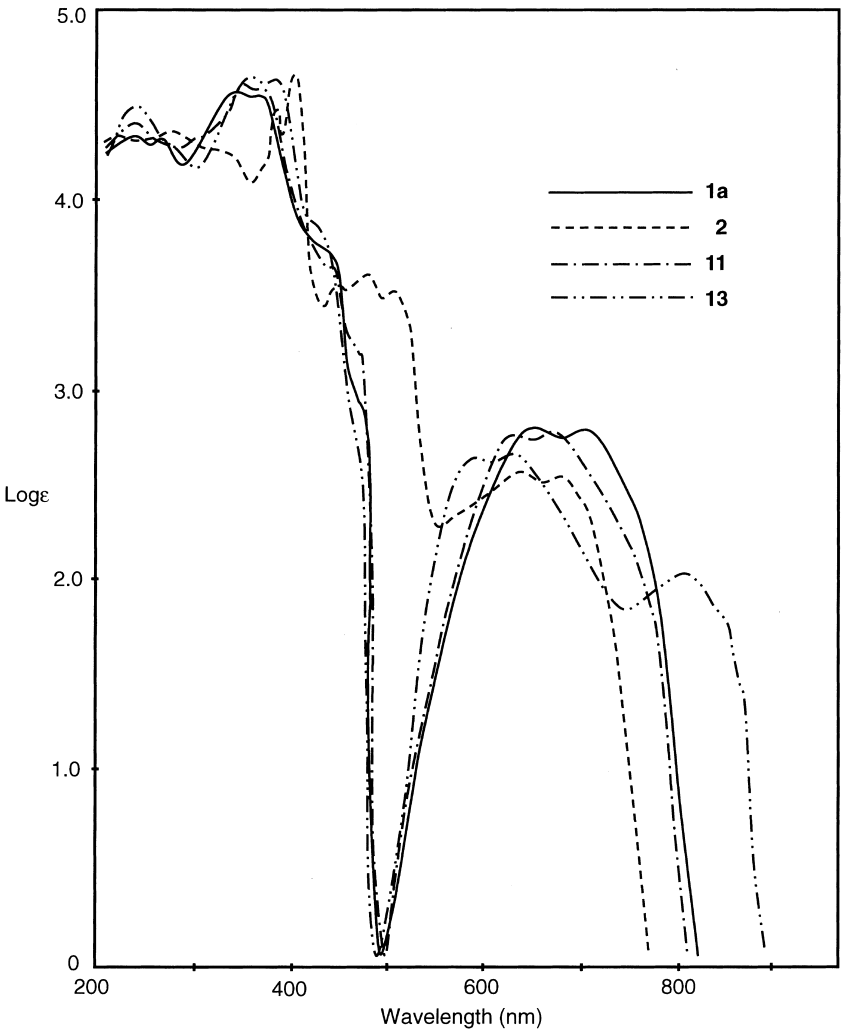
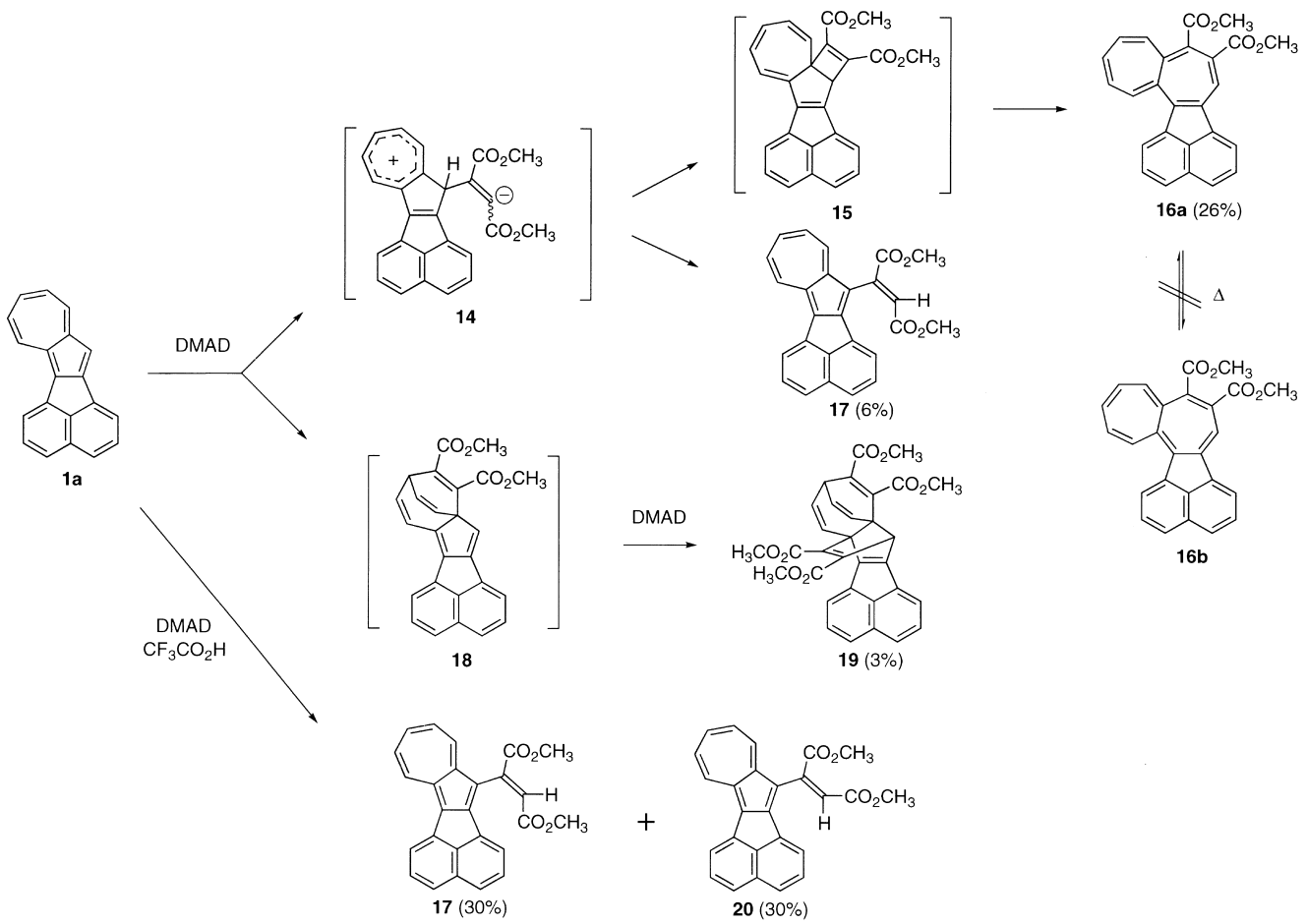


Chart 1. UV–vis absorption spectra of **1a**, **2**, **11** and **13** in CH_2Cl_2.

and the *E*-isomer of 7-substituted compound **17** in 26, 3, and 6% yields, respectively (Scheme 4). The reaction under similar conditions in the presence of CF_3CO_2H[16] gave a 1:1 mixture of *E*- and *Z*- 7-substituted products **17** and **20** in 60% yield without any cycloadducts.[18] The structures of **16a**, **17**, **19** and **20** were supported by the spectral and analytical data except the stereochemical configuration of **19**. The proton signals of the heptalene moiety of **16a** except those for H-7 (8.19 ppm) appear at the olefinic region between 5.86 and 6.62 ppm. The $^3J_{H-H}$ coupling constants of H10–H11 and H13–H14 are 10.7 and 6.6 Hz, respectively. Thus, the difference between them is large enough to conclude that clear double bond fixation exists in the pentalene part of **1a**. The structure of **16a** is further confirmed by X-ray crystallographical analysis. The ORTEP drawing of **16a** is shown in Figure 9. There are two independent molecules in the crystal of **16a** with a slight difference in the bond lengths and torsion angles. It is noteworthy that one (from C-9a to C-14a via C-12) of the seven-membered rings in **16a** surprisingly bends over the surface of the acenaphthylene ring with a large interplanar angle of 65.3° (average of the two molecules in the crystal) between the least-squares planes of those ring. This interplanar angle is far greater than that observed at the corresponding position in the cycloadduct between azulene itself and DMAD, reported by Hafner.[16] This anomalous bending of the heptalene ring in **16a** may be owing to steric repulsion between the hydrogens at the 14-position of heptalene and at the 1-position of the naphthalene. Also, difference in average bond lengths of the heptalene ring is observed to be ca. 0.1 Å in the crystal molecules, that indicates the localization of the double bond as shown in the structure of **16a** depicted in Scheme 4. The structure of **19** was also elucidated by X-ray crystallographic analysis. The ORTEP drawing of **19** is shown in Figure 10. It was revealed that two DMAD molecules are added to the surface of the azulene ring with anti stereochemical configuration. One of the methyl signals of four methoxycarbony groups in ^{1}H NMR of **19** appears at 2.63 ppm, while the others appear at 3.59, 3.76 and 3.77 ppm. In the X-ray structure of **19** one methyl group was found to locate on the naphthalene ring with the non-bonded atomic distance of 3.800 Å between this methyl and the C-15 carbons. That accounts for the high field shift of one of the methyl groups in the ^{1}H NMR spectrum of **19**. The Tables of fractional atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. 12 Union Road, Cambridge CB2 1EZ, United Kingdom (**16a**: CCDC 194348, **19**: CCDC 194347). The plausible reaction mechanisms of the formation of the products, **16a**, **17** and



Scheme 4. The reactions of **1a** with DMAD.

19, are shown in Scheme 4. As has been pointed out by Hafner[16] and Hansen,[17] **16a** presumably forms via a dipolar intermediate **14** and the [2+2] cycloadduct **15** stepwise. The former intermediate may also account for the formation of **17** by its proton transfer in either inter- or intramolecular way, though the geometrical selectivity forming only the *E*-isomer has not been clarified yet. The 1:2 adduct **19** can form via either the 1:1 adduct **18** or **21**. Calculations at the PM3 level of theory predict that **21** should be disfavored relative to **18** by ca. 23 kcal/mol (Fig. 11). Although a double bond shift of the heptalenes has been reported to occur with heats of activation enthalpy of 14.7 kJ/mol,[19] **16a** was found to be reluctant to that even in refluxing decaline. The large bending of the heptalene ring in **16a**

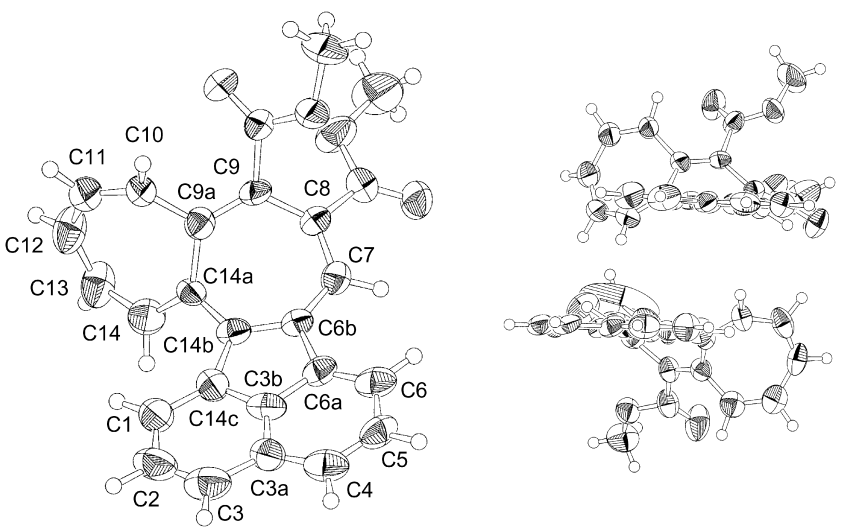


Figure 9. ORTEP drawing of one of two independent molecules in the crystal of **16a** (left). The drawings of the two in the crystal (right).

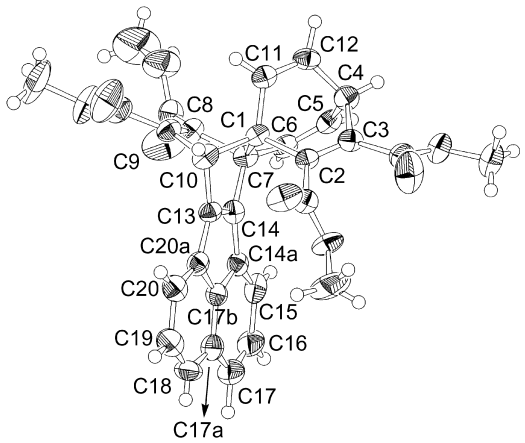


Figure 10. ORTEP drawing of **19**.

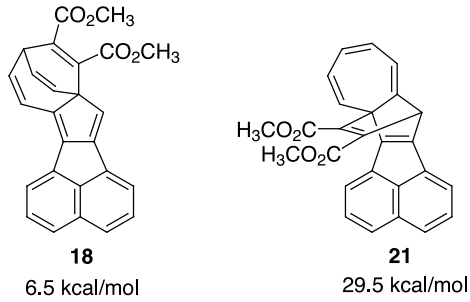


Figure 11. The heats of formation of **18** and **21** calculated by the PM3 method.

might be one reason for this reluctance fact. Thus, **16a** behaves as if it comprised vinylheptafulvene and acenaphthylene rather than heptalene and naphthalene.

3. Conclusion

We have synthesized azuleno[1,2-*a*]acenaphtylene (**1a**) with enamine **5** and 2*H*-cyclohepta[*b*]furan-2-one (**6**) by method of the Takase–Yasunami azulene synthesis. The spectral data and X-ray crystallographical analysis strengthen the conclusion that **1a** consists of azulene and naphthalene rather than acenaphtylene and heptafulvene in accordance with speculation drawn from the DEPE calculations. Also, electrophiric reactions of **1a** show reactivities of both azulene and naphthalene. The cycloaddition of **1a** with DMAD provided the adducts **16a** and **19**, whose solid-state structures were also elucidated.

4. Experimental

4.1. General

Melting points were measured on a Yanako MP-3 and are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum RX I spectrometer. UV spectra were measured on a Shimadzu UV-1600 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with tetramethylsilane as an internal standard on a JEOL α400. Mass spectra were measured on a JEOL GC-Mate mass spectrometer. The density functional calculations were done by using the MULLIKEN (ver. 2.0.0, 1995, IBM Co.) on an IBM RS/6000-397 computer.

4.1.1. 1-Pyrrolidinylacenaphthylene (5). To a solution of 1.00 g (5.95 mmol) of acenaphthen-1-one (**4**) in 10 mL of dry benzene was added 1.27 g (17.9 mmol) of pyrrolidine in the presence of 1.00 g of Zeolum® at room temperature. After being stirred at rt for 12 h the reaction mixture was filtered, and the solids are washed with 5 mL of dry benzene three times. The combined filtrate was concentrated to dryness to give 1.29 g (100%) of dark reddish oil of **5**. This oil was used in the next reaction without further purification. ^{1}H NMR ($CDCl_3$–TMS) δ=2.03 (m, 4H), 3.68 (m, 4H), 5.37 (s, 1H), 7.11 (d, J=6.8 Hz, 1H), 7.35 (dd, J=8.1, 6.8 Hz, 1H), 7.36 (d, J=8.1 Hz, 1H), 7.52 (dd, J=8.1, 6.8 Hz, 1H), 7.78 (d, J=8.1 Hz, 1H), 7.81 (d, J=6.8 Hz, 1H): ^{13}C NMR ($CDCl_3$–TMS) δ=151.9, 143.1, 136.6, 129.6, 129.2, 128.8, 128.7, 127.7, 124.9, 121.3, 117.5, 93.7, 50.9, 26.3.

4.1.2. Azuleno[1,2-*a*]acenaphthylne (1a). To a solution of 1.20 g (5.43 mmol) of **5** in 5 mL of dry xylene was added 0.79 g (5.43 mmol) of 2*H*-cyclohepta[*b*]furan-2-one (**6**). After being refluxed for 4 h, the reaction mixture was cooled to room temperature. Then, this mixture was directly chromatographed on silica gel with hexane as eluent to give 1.26 g (70%) of **1a**. Dark green needles, mp 155–156°C, IR (KBr) ν_{max} 3040w, 1609w, 1563m, 1393m, 830s, 772s, 736m, 716s cm^{-1}: ^{1}H NMR ($CDCl_3$–TMS) δ=7.05 (dd, J=10.0, 9.3 Hz, 1H, H-9),7.08 (t, J=10.0 Hz, 1H, H-11), 7.40 (t, J=10.0 Hz, 1H, H-10), 7.47 (s, 1H, H-7), 7.54 (dd, J=8.1, 6.8 Hz, 1H, H-5), 7.55 (dd, J=8.1, 6.8 Hz, 1H, H-2), 7.61 (d, J=8.1 Hz, 1H, H-3), 7.75 (d, J=8.1 Hz, 1H, H-4), 7.85 (d, J=6.8 Hz, 1H, H-1), 7.89 (d, J=6.8 Hz, 1H, H-6), 8.13 (d, J=9.3 Hz, 1H, H-8), 8.50 (d, J=10.0 Hz, 1H, H-12): ^{13}C NMR ($CDCl_3$–TMS) δ=153.8, 148.9, 139.4, 136.4, 136.4, 134.8, 133.9, 133.6, 132.7, 130.9, 130.6, 128.3, 127.8, 127.5, 124.5, 124.1, 123.8, 122.2, 118.9, 109.9: UV–vis (CH_2Cl_2) λ_{max} 223 (log ε=4.41) (nm), 288 (4.33), 310 (4.44), 340 (4.66), 353 (4.62), 404 (3.92), 427sh (3.76), 454sh (3.26), 625 (2.29), 675 (2.78), 740sh (2.41): MS *m*/*z* (70 eV) 252 (M^+, 100), 126 (12.5): HRMS: found: *m*/*z* 252.0943. Calcd for $C_{20}H_{12}$: 252.0938. Anal. found: C, 95.26; H, 4.96. Calcd for $C_{20}H_{12}$: C, 95.21; H, 4.79.

4.2. The thermal rearrangement of 1a

A solution of 0.10 g (0.40 mmol) of **1a** in 10 mL of benzene was passed through a hot quarts tube (1.5 mmϕ×260 mm) at a rate of 120 mL/min at 600°C and the pyrolysate was trapped by cold traps at temperature of liquid nitrogen. The pyrolysate was chromatographed on silica gel with 5% benzene–hexane as eluent to give 0.028 g (28%) of **9**, 0.014 g (14%) of **10**, and 0.058 g (58%) of **1a**. Compound **9**: pale yellow needles, benz[*j*]fluoranthene CAS registry number 205-82-3. Compound **10**: pale yellow needles, benz[*k*]fluoranthene, CAS registry number 207-08-9.

4.2.1. 7-Bromoazuleno[1,2-*a*]acenaphthylne (11). A solution of 0.12 g (0.78 mmol) of Br_2 in 5 mL of CH_2Cl_2 was added dropwise to a solution of 0.20 g (0.79 mmol) of **1a** in 20 mL of CH_2Cl_2 in the presence of 0.08 g

(0.78 mmol) of triethylamine at 5°C in a time period of 10 min. After being stirred at room temperature for 2 h, the reaction mixture was poured into 20 mL of water and extracted with CH_2Cl_2 (10 mL×2). The combined organic layer was washed with water and brine, and then was dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel with 30% benzene–hexane as eluent to give 0.26 g (96%) of **11**. Dark green needles, mp 178–179°C, IR (KBr) ν_{max} 3050w, 1570m, 1480m, 1410m, 1380m, 1280m, 800m, 770s, 738m, 712m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=7.16 (t, J=9.8 Hz, 1H, H-11), 7.20 (ddm, J=10.0, 9.8 Hz, 1H, H-9), 7.50 (t, J=9.8 Hz, 1H, H-10), 7.60 (dd, J=8.1, 6.8 Hz, 1H, H-2), 7.65 (dd, J=8.1, 6.8 Hz, 1H, H-5), 7.69 (d, J=8.1 Hz, 1H, H-3), 7.85 (d, J=8.1 Hz, 1H, H-4), 7.91 (d, J=6.8 Hz, 1H, H-1), 8.23 (dd, J=10.0, 0.7 Hz, 1H, H-8), 8.24 (d, J=6.8 Hz, 1H, H-6), 8.51 (d, J=9.8 Hz, 1H, H-12): ^{13}C NMR ($CDCl_3$–TMS) δ=151.4, 143.7, 138.7, 137.8, 136.4, 134.2, 133.9, 132.6, 131.5, 130.7, 130.5, 128.4, 128.2, 128.0, 124.7, 124.6, 124.4, 122.9, 119.4, 97.6: UV/vis (CH_2Cl_2) λ_{max} 236 (log ε=4.39) (nm), 263 (4.31), 342 (4.60), 428sh (3.77), 455sh (3.30), 643 (2.81), 696 (2.82): MS m/z (70 eV) 330, 332 (M^+, 99.8, 100), 250 (M^+−HBr, 59.7), 125 (38.0): HRMS: found: m/z 330.0049, 332.0024. Calcd for $C_{20}H_{11}Br$: 330.0044, 332.0024. Anal. found: C, 72.27; H, 3.35. Calcd for $C_{20}H_{11}Br$: C, 72.53; H, 3.35.

4.2.2. 3,7-Dibromoazuleno[1,2-*a*]acenaphthylene (12). A solution of 0.07 g (0.44 mmol) of Br_2 in 5 mL of CH_2Cl_2 was added dropwise to a solution of 0.15 g (0.45 mmol) of **11** in 20 mL of CH_2Cl_2 in the presence of 0.04 g (0.44 mmol) of triethylamine at 5°C in a time period of 10 min. After being stirred at room temperature for 2 h, the reaction mixture was poured into 20 mL of water and extracted with CH_2Cl_2 (10 mL×2). The combined organic layer was washed with water and brine, and then was dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel with 30% benzene–hexane as eluent to give 0.19 g (94%) of **12**. Dark green needles, mp 228–229°C, IR (KBr) ν_{max} 3016w, 1571m, 1414m, 1381s, 1349m, 815s, 768m, 736s, 712m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=7.13 (t, J=9.8 Hz, 1H, H-11), 7.18 (dd, J=9.8, 9.3 Hz, 1H, H-9), 7.48 (t, J=9.8 Hz, 1H, H-10), 7.62 (d, J=7.3 Hz, 1H, H-1), 7.67 (dd, J=8.3, 6.8 Hz, 1H, H-5), 7.74 (d, J=7.3 Hz, 1H, H-2), 7.98 (d, J=8.3 Hz, 1H, H-4), 8.18 (d, J=6.8 Hz, 1H, H-6), 8.19 (d, J=9.3 Hz, 1H, H-8), 8.36 (d, J=9.8 Hz, 1H, H-12): ^{13}C NMR ($CDCl_3$–TMS) δ=151.1, 144.2, 140.2, 138.1, 135.8, 134.3, 134.0, 133.3, 131.7, 131.3, 130.7, 130.5, 129.1, 127.5, 125.1, 124.8, 123.6, 119.8, 119.5, 98.2: UV/vis (CH_2Cl_2) λ_{max} 228 (log ε=4.51) (nm), 298 (4.35), 317 (4.45), 346 (4.67), 364 (4.59), 414sh (3.98), 439sh (3.92), 465sh (3.67), 647 (2.94), 696 (2.96), 762 (2.62): MS m/z (70 eV) 408, 410, 412 (M^+, 52.3, 100, 53.2), 330, 332 (M^+−Br, 12.3, 10.9), 250 (M^+−Br_2, 58.7): Anal. found: C, 58.78; H, 2.55. Calcd for $C_{20}H_{10}Br_2$: C, 58.57; H, 2.46.

4.2.3. Azuleno[1,2-*a*]acenaphthylene-7-carboaldehyde (13) with $POCl_3$-DMF. To a solution of 0.20 g (0.79 mmol) of **1a** in 20 mL of dimethylformamide at 5°C was added dropwise 0.12 g (0.79 mmol) of $POCl_3$ in a time period of 10 min. After being refluxed for 2 h, the reaction mixture was cooled to room temperature. Then, the reaction mixture was poured into 20 mL of water and extracted with CH_2Cl_2 (10 mL×2). The combined organic layer was washed with aq. $NaHCO_3$ and brine, and then was dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel with $CHCl_3$ as eluent to give 0.007 g (3%) of **13**.

4.2.4. Compound 13 with triethyl orthoformate in the presence of boron trifluoride diethyl etherate. A solution of 0.12 g (0.79 mmol) of triethyl orthoformate in 5 mL of CH_2Cl_2 was added dropwise to a solution of 0.20 g (0.79 mmol) of **1a** in 20 mL of CH_2Cl_2 in the presence of 0.10 mL (0.79 mmol) of boron trifluoride diethyl etherate at 5°C. After being stirred at room temperature for 1 h, the reaction mixture was poured into 20 mL of water and extracted with CH_2Cl_2 (10 mL×2). The combined organic layer was washed with aq. $NaHCO_3$ and brine, and then was dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel with $CHCl_3$ as eluent to give 0.22 g (84%) of **13**. Dark green needles, mp 179–180°C, IR (KBr) ν_{max} 3040w, 2950w, 1600s, 1420m, 1290m, 1080m, 830s, 520s cm^{-1}: ^1H NMR (d-DMSO-TMS) δ=7.70 (dd, J=10.3, 9.8 Hz, 1H, H-9), 7.73 (dd, J=9.8, 9.3 Hz, 1H, H-11), 7.75 (dd, J=8.1, 6.8 Hz, 1H, H-2), 7.82 (dd, J=8.1, 6.8 Hz, 1H, H-5), 7.94 (d, J=8.1 Hz, 1H, H-3), 7.97 (t, J=9.8 Hz, 1H, H-10), 8.11 (d, J=8.1 Hz, 1H, H-4), 8.37 (d, J=6.8 Hz, 1H, H-1), 8.74 (d, J=6.8 Hz, 1H, H-6), 9.10 (d, J=9.3 Hz, 1H, H-12), 9.35 (d, J=10.3 Hz, 1H, H-8), 10.85 (s, −CHO): ^{13}C NMR (d-DMSO-TMS) δ=184.6, 153.5, 148.3, 139.7, 137.4, 136.3, 136.0, 134.4, 132.5, 132.0, 129.8, 129.8, 129.6, 129.6, 128.5, 128.4, 126.8, 125.7, 125.6, 121.3, 118.9: UV/vis (CH_2Cl_2) λ_{max} 239 (log ε=4.51) (nm), 269 (4.31), 352 (4.68), 376 (4.74), 418sh (3.95), 583 (2.74), 624 (2.72), 776 (2.01), 833 (2.03), 866sh (1.64), 878sh (1.31): MS m/z (70 eV) 280 (M^+, 100), 250 (47.8): HRMS: found: m/z 280.0881. Calcd for $C_{21}H_{12}O$: 280.0886. Anal. found: C, 89.97; H, 4.49. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.31.

4.2.5. The reaction of 1a with DMAD. A solution of 0.30 g (1.19 mmol) of **1a** and 0.27 g (1.19 mmol) of DMAD in 5 mL of dry xylene was refluxed for 4 h. The reaction mixture was cooled to room temperature and then was directly chromatographed on silica gel with 20% AcOEt–hexane as eluent to give 0.12 g (26%) of **16a** and 0.03 g (6%) of **17**, with 50% AcOEt–hexane as eluent to give 0.02 g (3%) of **19**. Compound **16a**: dark red needles, mp 217–218°C, IR (KBr) ν_{max} 3030w, 2940w, 1720s, 1580m, 1430s, 1320m, 1280m, 1240m, 1120m, 1080m, 820m, 768s, 720m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=3.67 (s, −OMe), 3.80 (s, −OMe), 5.86 (d, J=10.7 Hz, 1H, H-10), 6.21 (d, J=6.6 Hz, 1H, H-14), 6.34 (dd, J=10.7, 6.6 Hz, 1H, H-11), 6.53 (dd, J=11.1, 6.6 Hz, 1H, H-12), 6.62 (dd, J=11.1, 6.6 Hz, 1H, H-13), 7.57 (dd, J=8.2, 6.9 Hz, 1H, H-2), 7.64 (dd, J=8.2, 6.9 Hz, 1H, H-5), 7.75 (d, J=6.9 Hz, 1H, H-1), 7.83 (d, J=6.9 Hz, 1H, H-6), 7.90 (d, J=8.2 Hz, 1H, H-4), 7.91 (d, J=8.2 Hz, 1H, H-3), 8.19 (bs, 1H, H-7): ^{13}C NMR ($CDCl_3$–TMS) δ=167.6, 167.5, 143.4, 142.7, 137.9, 137.8, 137.1, 136.3, 135.0, 132.8, 132.0, 131.4, 130.5, 130.2, 129.2, 128.8, 128.6, 128.4, 128.1, 128.0, 125.5, 124.9, 123.4, 122.8, 52.3, 51.8: UV/vis (CH_2Cl_2) λ_{max} 212 (log ε=4.26) (nm), 228 (4.48), 336 (4.31), 515 (3.06): MS

m/z (70 eV) 394 (M^+, 100), 379 (27.9), 363 (12.6): HRMS: found: *m/z* 394.1206. Calcd for $C_{26}H_{18}O_4$: 394.1205. Anal. found: C, 79.10; H, 4.76. Calcd for $C_{26}H_{18}O_4$: C, 79.18; H, 4.60. **17**: dark brown needles, mp 163–164°C, IR (KBr) ν_{max} 3031w, 2952w, 1734s, 1721s, 1625m, 1568m, 1482m, 1433s, 1418m, 1386m, 1317m, 1287m, 1252s, 1202m, 1177m, 1021m, 881m, 819m, 766s, 711m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=3.40 (s, –OMe), 3.74 (s, –OMe), 7.11 (ddm, *J*=9.8, 9.5 Hz, 1H, H-9), 7.18 (t, *J*=9.8 Hz, 1H, H-11), 7.39 (s, 1H), 7.47 (t, *J*=9.8 Hz, 1H, H-10), 7.53 (dd, *J*=8.3, 6.8 Hz, 1H, H-2), 7.57 (dd, *J*=8.3, 6.8 Hz, 1H, H-5), 7.65 (d, *J*=8.3 Hz, 2H, H-3, -4), 7.78 (d, *J*=6.8 Hz, 1H, H-1), 7.90 (dd, *J*=9.5, 0.7 Hz, 1H, H-8), 7.93 (d, *J*=6.8 Hz, 1H, H-6), 8.58 (d, *J*=9.8 Hz, 1H, H-12): ^{13}C NMR ($CDCl_3$–TMS) δ=167.4, 165.5, 152.7, 145.7, 139.3, 139.1, 137.2, 134.4, 134.4, 134.3, 133.6, 132.0, 131.7, 130.5, 130.1, 128.3, 127.9, 127.9, 125.2, 124.9, 124.5, 122.8, 119.4, 115.5, 53.0, 51.9: UV/vis (CH_2Cl_2) λ_{max} 228 (log ε=4.49) (nm), 343 (4.59), 364 (4.62), 406 (3.95), 427 (3.87), 454 (3.51), 630 (2.79), 681 (2.78), 744sh (2.41): MS *m/z* (70 eV) 394 (M^+, 100), 335 (36.9), 323 (41.9), 276 (69.8): Anal. found: C, 79.33; H, 4.81. Calcd for $C_{26}H_{18}O_4$: C, 79.18; H, 4.60. Compound **19**: orange needles, mp 242–243°C, IR (KBr) ν_{max} 3038w, 2997w, 2950w, 1726s, 1714s, 1619m, 1432m, 1271s, 1259s, 1210m, 1102m, 1056m, 820m, 773m, 751m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=2.63 (s, –OMe), 3.59 (s, –OMe), 3.76 (s, –OMe), 3.77 (s, –OMe), 3.78 (t-like, *J*=6.8 Hz, 1H, H-4), 4.90 (s, 1H, H-10), 6.13 (d, *J*=10.5 Hz, 1H, H-6), 6.44 (d, *J*=7.9 Hz, 1H, H-11), 6.46 (dd, *J*=10.5, 6.8 Hz, 1H, H-5), 6.65 (dd, *J*=7.9, 6.8 Hz, 1H, H-12), 7.46 (dd, *J*=8.3, 6.8 Hz, 1H, H-16), 7.48 (dd, *J*=8.3, 6.8 Hz, 1H, H-19), 7.54 (d, *J*=6.8 Hz, 1H, H-15), 7.65 (d, *J*=6.8 Hz, 1H, H-20), 7.70 (d, *J*=8.3 Hz, 1H, H-17), 7.73 (d, *J*=8.3 Hz, 1H, H-18): ^{13}C NMR ($CDCl_3$–TMS) δ=166.6, 165.2, 164.9, 164.2, 156.4, 155.6, 153.3, 147.0, 143.8, 142.5, 138.5, 134.0, 133.7, 132.5, 132.3, 130.6, 128.5, 128.0, 127.7, 127.5, 127.1, 123.5, 123.1, 123.0, 92.8, 64.5, 54.1, 52.3, 52.2, 52.1, 51.1, 37.2: UV/vis (CH_2Cl_2) λ_{max} 228 (log ε=4.57) (nm), 293 (3.84), 333 (4.13), 435 (2.49): MS *m/z* (70 eV) 536 (M^+, 11.6), 477 (30.9), 445 (33.5), 415 (75.7), 300 (32.9): Anal. found: C, 71.59; H, 4.53. Calcd for $C_{32}H_{24}O_8$: C, 71.64; H, 4.51.

4.2.6. The reaction of 1a with DMAD in the presence of CF_3CO_2H. To a solution of 0.20 g (0.79 mmol) of **1a** and 0.09 g (0.79 mmol) of trifluoroacetic acid in 5 mL of dry xylene was added 0.11 g (0.79 mmol) of DMAD and this mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and then was chromatographed on silica gel with 15% AcOEt–hexane as eluent to give 0.31 g (30%) of **17** and 0.31 g (30%) of **20**. **20**: dark blue needles, mp 163–164°C, IR (KBr) ν_{max} 3049w, 3029w, 2993w, 2946w, 1730s, 1714s, 1594s, 1571m, 1431m, 1410m, 1336m, 1308m, 1247s, 1194m, 1161s, 822m, 772m, 709m cm^{-1}: ^1H NMR ($CDCl_3$–TMS) δ=3.87 (s, –OMe), 3.89 (s, –OMe), 6.43 (s, 1H), 7.17 (m, 2H, H-9, –H), 7.48 (t, *J*=9.8 Hz, 1H, H-10), 7.56 (dd, *J*=8.3, 6.8 Hz, 1H, H-2), 7.58 (dd, *J*=8.3, 6.8 Hz, 1H, H-5), 7.66 (d, *J*=8.3 Hz, 1H, H-3), 7.80 (d, *J*=8.3 Hz, 1H, H-4), 7.90 (d, *J*=6.8 Hz, 1H, H-1), 8.16 (d, *J*=6.8 Hz, 1H, H-6), 8.37 (d, *J*=9.3 Hz, 1H, H-8), 8.55 (d, *J*=9.8 Hz, 1H, H-12): ^{13}C NMR ($CDCl_3$–TMS) δ=168.2, 165.6, 151.9, 145.9, 144.0, 139.1, 137.8, 135.3, 134.5, 133.6, 132.9, 132.9, 132.3, 130.4, 128.3, 128.1, 128.0, 126.1, 125.5, 124.9, 124.2, 122.7, 119.6, 116.5, 52.7, 52.1: UV/vis (CH_2Cl_2) λ_{max} 239 (log ε=4.46) (nm), 267 (4.32), 365 (4.72), 404 (4.05), 425 (3.98), 627 (2.81), 674 (2.81), 736 (2.46): MS *m/z* (70 eV) 394 (M^+, 100), 335 (31.7), 320 (18.3), 276 (56.2): Anal. found: C, 79.11; H, 4.72. Calcd for $C_{26}H_{18}O_4$: C, 79.18; H, 4.60.

4.3. Computations

Ab initio molecular orbital calculations were performed using the MULLIKEN (ver. 2.0.0, 1995, IBM Co.) on an IBM RS/6000-397 computer on **1a**. The MB3LYP (Mbecke3LYP) functional in MULLIKEN uses the local correlation function of Perdew and Wang[20] instead of the Vosko, Wilk, and Nusair functional,[21] and is very similar to the Becke3LYP density by Stephens et al.[22] Semiempirical molecular orbital calculations were performed using the CAChe MOPAC program with the PM3 method[23] on **1a**, **11**, **11H$^+$a**, **11H$^+$b**, **11H$^+$c**, **18**, and **21**.

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