Tetrahedron Vol. 49, No 11, pp 2201-2208, 1993
Printed in Great Britain

0040-4020/93 $6 00+.00

STRAINED DOUBLE BONDS IN TWO TYPES OF POLYCYCLIC HYDROCARBONS

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(*Received in Japan* 26 *November* 1992)

Abstract: Two polycyclic compounds **1** and **2** with pyramidalized double bond are prepared from their corresponding halides. Both of them are stable at ambient temperature but gradually transform to the epoxides upon exposing to air. Cycloaddition with either anthracene or cyclopentadiene yield the corresponding [4 + 2] adducts.

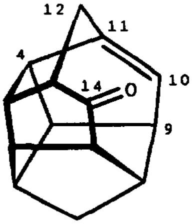
INTRODUCTION

Binor-S (heptacyclo[$8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}$]tetradecane) and the cage-shaped molecule heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane[1] are dimers of norbornadiene which can be synthesized directly upon metal-catalysis.[2] Selective ring openings of these compounds produce polycyclic hydrocarbons which are of special interests among both theoretical and synthetic chemists.[3] In this report we describe the preparation of two strained olefins derived from these two types of compounds where the double bonds are pyramidalized as constrained by their rigid skeletons.

RESULTS AND DISCUSSION

Both the olefins **1** (hexacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}$]tetradecan-10-en-14-one) and **2** ($\Delta^{1,14}$-hexacyclo[$9.2.1.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}$]-tetradecene) are produced by dehydrohalogenation of the corresponding secondary halides. Compound **1** was prepared from **3a**[4] in quantitative yield upon treatment with DBN in refluxed toluene for 20 hours. After purification the olefin can be stored under nitrogen at ambient temperature, yet it is gradually oxidized while exposed to air. The presence of double bond in **1** is clearly shown in the ^{1}H NMR spectra by the broad singlet at δ 5.00 (1H, br) and in ^{13}C by the two peaks at δ 127.7 (C10) and 148.1 (C11). In IR it gives two absorptions at 1616 (w) and 1719 (s) cm^{-1}, the former being assigned to the stretching of the pyramidalized double bond.[5] This value is red shifted by 60 cm^{-1} as compared with the normal trimethyl-substituted ethylene (i.e. 2-methyl-2-butene).[6] It is quite close to the value predicted by semiempirical models[8] (ca. 1629 cm^{-1} based on PM3[7]), and this value is confirmed by the absorption of Raman at 1623 cm^{-1}.

Compound **2** was prepared from the bromide **4a**[9] in 75% yield under the same reaction condition. In ^{1}H NMR the olefinic proton resonates at δ 5.46 and in ^{13}C the two carbons at δ 136.3 (d) and 144.7 (s), however, no absorption is observable in IR between 1550-1650 cm^{-1} (C=C stretching predicted at ca. 1593 cm^{-1}). This compound is also stable at ambient temperature while kept under nitrogen.



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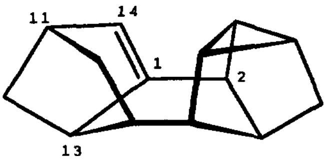

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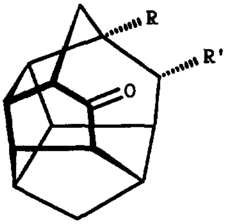
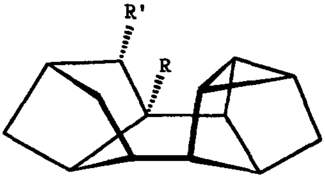


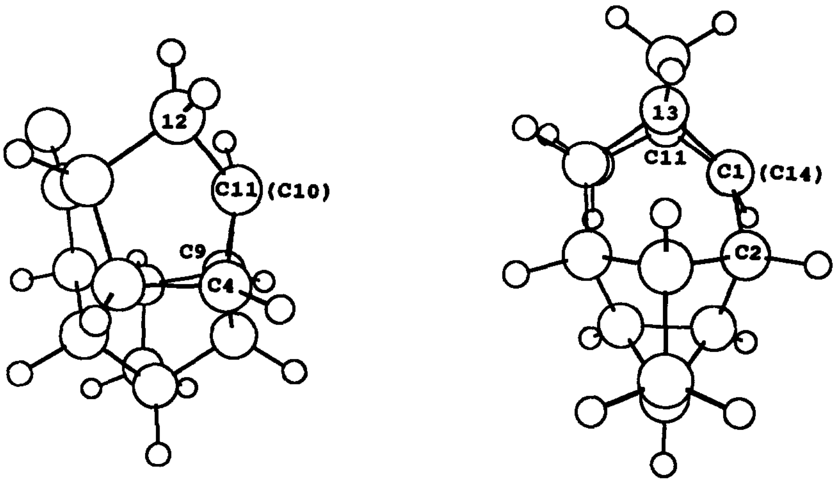
3 a) R = H, R'= I
b) R,R'= O
c) R = R'= H



4 a) R = H, R'= Br
b) R,R'= O
c) R = R'= H

For olefin **1**, the angle formed by planes C12-C11-C10 and C4-C11-C10 is estimated to be 135° by MM2(91)[10] and that by C12-C11-C10 and C9-C10-C11 to be 132°. Likewise for olefin **2**, the angle between planes C2-C1-C14 and C13-C1-C14 is 143° and that between C2-C1-C14 and C1-C14-C11 is 137°. A figure showing the projections along the double bonds of **1** and **2** is presented in Figure 1. The estimated olefin strain energies are 10.6 kcal/mole for **1** and 10.7 kcal/mole for **2**, both are well below the instability limit (17 kcal/mole) proposed by Schleyer.[11] The ^1H-^{13}C coupling constant for the tertiary carbon (C10) of **1** is measured to be 161.4 Hz, which is close to the standard value for sp^2 hybridization. Although stable in the absence of oxygen, they gradually transform to the corresponding epoxides in air. The structures of **3b** and **4b** are confirmed by comparing with authentic samples prepared by reacting **1** and **2** with m-chloroperbenzoic acid. The epoxy carbons of **3b** are designated in ^{13}C by the absorptions at δ 66.6 (d) and 74.2 (s), whereas those of **4b** at δ 58.9 (d) and 60.7 (s).

The strained double bonds are reactive toward hydrogenation as well as cycloaddition reactions. In methanol upon the catalysis of Pd/C both **1** and **2** are reduced to the corresponding saturated products **3c** and **4c**.[9] The spectroscopic features of both products are identical to those of the known structures. For cycloaddition reactions the thermally allowed $[_\pi 4_s + {}_\pi 2_s]$ mode proceeds smoothly upon heating with both anthracene and

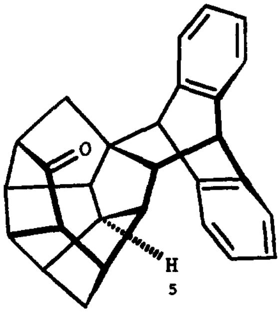


1 2

Figure 1. Projections along the double bonds of **1** (C11 -> C10) and **2** (C1 -> C14) showing the distortions at the quaternary carbons.

cyclopentadiene. The purified anthracene adducts **5** and **6** are collected in 80% and 60% yields respectively, while the cyclopentadiene adduct **7** is isolated in 74%. In the latter reaction the *endo* or *exo* geometry of **7** is not yet clear.

In the analysis of ^{1}H NMR spectra of **5** and **6** an interesting structural detail of these compounds is disclosed. During the processes of dehydrohalogenation of **3a** and **4a**, it is also possible to produce the isomeric olefins for both **1** and **2**, i.e. the $\Delta^{9,10}$-isomer of **1** and the $\Delta^{11,14}$-isomer of **2**. Within each pair of isomers, the position of the double bond can not be readily established due to the high similarity of their spectroscopic features. However, in the anthracene adducts **5** and **6**, the fused benzene moieties are orientated so that some of the hydrogen nucleus appear within the induced diamagnetic regions. The abnormal up-field shifts of these hydrogens can be used as tags to identify the



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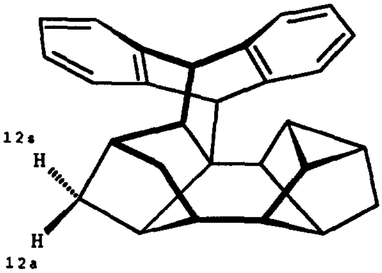

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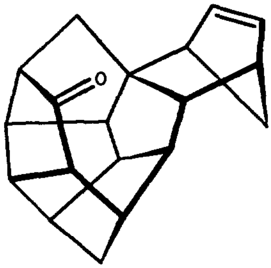

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carbons where anthracene are fused to, and where the original double bond was located. For **6** the two resonances in ^{1}H at δ -0.40 (dm, J = 11 Hz) and 0.39 (dm, J = 11 Hz) are assigned to H(12s) and H(12a) accordingly, whereas for **5** the multiplet at δ 1.0 is assigned to H(5).[12] A simple modeling study of **5** indicates that the averaged distance of H(5)-C(phenyl) is 3.28 Å. This value is much shorter than the corresponding distance of H(4)-C(phenyl) in the $\Delta^{9,10}$-isomer of **5**, where 4.59 Å is estimated. For this reason the $\Delta^{9,10}$-isomer of **5**, if obtained, can not satisfactorily explain the observed unusual up-field hydrogen shift. The assignments for all the NMR signals of **5** are then resolved using the 2D COSY and the ^{1}H-^{13}C HMBC[13] techniques.

Force-field calculation (MM2) indicates that the heat of formation of **1** (7.8 kcal/mole) is slightly lower than that of the $\Delta^{9,10}$-isomer (10.2 kcal/mole). The theoretical prediction correlates very well with the result of experiment. It is interesting to note that this regio-preference of elimination, i.e. the deprotonation occurs at C(11) instead of at C(9), is again parallel to what has been observed previously for the enolization of **3a**.[14]

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained either on a Brucker AC-200 or an AMX-500 FT spectrometer. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 240C analyzer. Mass spectra were carried out on a VG Analytical 70-250 S/SE spectrometer. MM2(91) and MOPAC (version 6.0) programs were obtained from QCPE, Indiana University.

Hexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-10-en-14-one (1). A 50 mL round bottom flask containing a magnetic stirring bar fitted with a condenser was evacuated then flushed with nitrogen. To this flask under an atomsphere of nitrogen was added 14-iodohexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-10-one (**3a**)[4] (97 mg, 0.30 mmol), followed by freshly distilled toluene (20 mL) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.40 mL). The toluene solution was stirred and heated to reflux for 20 h. The resulting mixture was evaporated *in vacuo*, and was purified by passing through a silica-gel flash column chromatography eluted with n-hexane/ethyl acetate (v/v 9/1). The olefin **1** was collected as white solids in nearly a quantitative yield (60 mg, 0.30 mmol). ^{1}H NMR ($CDCl_3$), δ 1.55 (br, 2H), 2.32-2.51 (m, 3H), 2.66-2.77 (m, 3H), 2.81-2.89 (m, 2H), 2.96 (d, J = 10 Hz, 1H), 3.06-3.11 (m, 1H), 3.38 (t, J = 9 Hz, 1H), 5.00 (br, 1H); ^{13}C NMR ($CDCl_3$), δ 41.59 (t), 42.69 (t), 44.05 (d), 46.18 (d), 46.68 (d), 49.69 (d), 52.54 (d), 55.86 (d), 56.96 (d), 57.27 (d), 59.64 (d), 127.71 (d), 148.14 (s), 225.39 (s); IR ($CHCl_3$) ν 3020 (s), 2962 (s), 2872 (w), 1719 (s), 1616 (w), 1512 (w), 1421 (w), 1373 (w), 1211 (s) cm^{-1}; MS (50 eV): m/z (rel. int.) 198 (M^+, 10%), 186 (100%), 172 (25%), 157 (80%), 119 (95%); HRMS calcd for $C_{16}H_{14}O$: 198.1045; found: 198.1042.

$\Delta^{1,14}$-hexacyclo[9.2.1.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}]tetradecene (2). The procedure was similar to that of the preparation of **1**. To a 25 mL flask was added 10-bromohexacyclo[9.2.1.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}]tetradecene (**4a**)[9] (78.8 mg, 0.30 mmol), freshly distilled toluene (10 mL), and DBN (0.42 mL). The solution was heated to reflux for 24 h, then the solvent was evaporated *in vacuo*. The products were separated by HPLC eluted with n-hexane to yield **2** as an oil (0.41 mg, 0.22 mmol, 75% yield). ^{1}H NMR ($CDCl_3$), δ 0.72 (t, J = 5 Hz, 1H), 0.69-1.12 (m, 3H), 1.19-1.32 (m, 4H), 1.51-1.62 (m, 1H), 1.75 (d, J = 11 Hz, 1H), 2.28 (m, 2H), 2.64 (br, 1H), 2.88 (m, 2H), 5.63 (s, 1H); ^{13}C NMR ($CDCl_3$), δ 13.95 (d), 17.74 (d), 21.71 (d), 32.37 (t), 32.54 (d), 34.42 (t), 38.22 (d), 38.52 (t), 42.95 (d), 43.91 (d), 44.13 (d), 46.39 (d), 136.32 (d), 144.74 (s); IR ($CHCl_3$) ν 3020 (s), 2968, 2868 (w), 1710 (w), 1521 (w), 1417 (w) cm^{-1}; MS (36 eV) m/z (rel. int.) 184 (M^+, 90%), 169 (100%), 155 (35%), 129 (50%), 91 (50%); HRMS calcd for $C_{14}H_{16}$: 184.1252; found: 184.1260.

10,11-Epoxyhexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-14-one (3b). The olefin **1** (100 mg, 0.50 mmol) was stirred with m-chloroperbenzoic acid (m-CPBA) (85%, 104 mg, 0.51 mmol) and $NaHCO_3$ (18 mg) in CH_2Cl_2 at room temperature for 1 h. The mixture was filtered through celite, and the filtrate was washed three times with saturated Na_2SO_3 solution followed by three times with saturated $NaHCO_3$ solution. The solution was dried over anhydrous $MgSO_4$, evaporated *in vacuo*, and the resulted mixture was passed through a silica gel flash column chromatography eluted with n-hexane/ethyl acetate (v/v 8/1). The epoxide **3b** was collected as white solids (98 mg, 0.46 mmol, 91%): mp 174-175 °C; ^{1}H NMR ($CDCl_3$), δ 1.72 & 1.73 (2s, 2H), 2.23 (d, J = 11 Hz, 1H), 2.44 (dd, J = 6 & 11 Hz, 1H), 2.53-2.68 (m, 2H), 2.69-2.78 (m, 3H), 2.84-2.95 (m, 4H), 3.03-3.12 (m, 1H); ^{13}C NMR ($CDCl_3$), δ 37.53 (t), 44.15 (t), 46.05 (d), 46.13 (d), 48.64 (d), 49.17 (d), 49.65 (d), 50.49 (d), 53.24 (d), 53.76 (d), 55.89 (d), 66.93 (d), 74.16 (s), 226.3 (s, CO); IR ($CDCl_3$) ν 2968, 2875 (w), 1723, 1457 (w), 1424 (w), 1384 (w), cm^{-1}; MS (40 eV): m/z (rel. int.) 214 (M^+, 10%), 186 (M^+-CO, 100%), 157 (80%), 119 (90%); HRMS calcd for $C_{16}H_{14}O_2$: 214.0994; found: 214.0998.

1,14-Epoxyhexacyclo[9.2.1.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}]tetradecene (4b). The procedure was similar to that of **3b**. The olefin **2** (27.4 mg, 0.15 mmol) was used to react with m-CPBA (85%, 34.6 mg, 0.20 mmol) and $NaHCO_3$ (25 mg) in CH_2Cl_2 (10 mL) at room temperature for 30 min. The product was worked up to yield **4b** as white solids (23.5 mg, 0.118 mmol, 78%). ^{1}H NMR ($CDCl_3$), δ 0.78 (dm, J = 11 Hz, 1H), 1.03-1.10 (m, 2H), 1.20-1.31 (m, 2H), 1.40-1.57 (m, 3H), 1.99 (dm, J = 9 Hz, 1H), 2.17-2.35 (m, 4H), 2.95 (s, 1H); ^{13}C NMR ($CDCl_3$), δ 14.88 (d), 17.61 (d), 18.89 (d), 26.68 (t), 30.72 (t), 33.82 (t), 34.32 (d), 36.41 (d), 37.57 (d), 38.74 (d), 41.07 (d), 42.91 (d), 58.87 (d), 60.70 (s); MS (28 eV) m/z (rel. int.) 200 (M^+, 10%), 169 (5%), 131 (10%), 84 (100%).

The hydrogenation of 1 and 2. The olefin **1** (51 mg, 0.25 mmol) was mixed with 10% Pd/C (10 mg) and methanol (30 mL), and the mixture was fitted to a Parr hydrogenator at 45 psi gas pressure. The reaction was completed in 3 h, the products were filtered then purified through a silica gel chromatograph eluted with n-hexane/ethyl acetate (v/v 8/1). The ketone **3c** was collected in 91% yield (46 mg, 0.23 mmol). ^{1}H NMR (CDC$_{13}$) δ 1.14 (dd, J= 3.5 & 15 Hz, 1H), 1.67 (s, 2H), 1.90-2.00 (m, 2H), 2.25 (d, J= 12 Hz, 1H), 2.38 (m, 2H), 2.52-2.78 (m, 6H), 2.95-3.03 (m, 2H). ^{13}C NMR (CDCl$_3$) δ 34.8 (t), 45.3 (t), 46.4 (t), 47.2 (d), 48.0 (d), 48.5 (d), 49.9 (d), 51.9 (d), 53.8 (d), 54.2 (d), 56.5 (d), 56.8 (d), 57.2 (d), 229.4 (s). MS (70 eV) m/z (relative intensity) 200 (M$^+$, 100%), 182 (2.3%), 172 (M$^+$-CO, 8.8%), 159 (3.9%), 143 (6.8%), 133 (10%), 129 (16%). IR (CDCl$_3$) 3017 (sh), 2995 (s), 2872 (sh), 1721 (s), 1462 (m) cm^{-1}. Anal. calcd for $C_{14}H_{16}O$: C 83.96, H 8.85; found: C 84.12, H 8.16. Compound **4c**[9] (yield 76%): ^{1}H NMR(CDC$_{13}$) δ 1.01 (d, J = 5 Hz, 2H), 1.10 (m, 1H), 1.23 (s, 2H), 1.33 (s, 2H), 1.12-1.58 (m, 4H), 1.79 (m, 1H), 1.87-1.97 (m, 3H), 2.10-2.06 (m, 3H). ^{13}C NMR (CDCl$_3$) δ 14.94 (d), 15.22 (d), 33.58 (t), 33.93 (d), 34.34 (t), 35.34 (d), 38.02 (d), 38.49 (d), 39.20 (t), 41.58 (d); MS (30 eV) m/z (rel. int.) 186 (M$^+$, 100%), 157 (30%), 129 (40%), 91 (50%).

Cycloaddition of 1 and 2 with anthracene. An equal molar amount of the olefin (**1** or **2**) and anthracene was heated in benzene (freshly distilled) to reflux for 6-12 h. The adducts were purified by column chromatography eluted with n-hexane/ethyl acetate to form white solids. Compound **5** (67% yield): mp 260-260.5 °C; ^{1}H NMR (CDCl$_3$), δ 1.00 (br m, 1H), 1.52 (AB pattern, J = 10, 18 Hz, 2H), 1.74 (d, J = 12.6 Hz, 1H), 1.91 (br, 1H), 1.97-2.07 (m, 2H), 2.48-2.53 (m, 2H), 2.56-2.62 (m, 3H), 2.67-2.75 (m, 1H), 3.13 (m, 1H), 3.81 (s, 1H), 4.01 (d, J = 3 Hz, 1H), 7.02-7.25 (m, 8H); ^{13}C NMR (CDCl$_3$), δ 45.53 (t), 46.23 (d), 48.08 (d), 50.45 (t), 51.46 (d), 52.24 (d), 53.24 (d), 53.29 (d), 54.18 (d), 55.28 (d), 55.84 (d), 56.51 (d), 56.73 (d), 61.26 (d), 67.02 (d), 123.53 (d), 123.80 (d), 124.17 (d), 124.86 (d), 125.51 (d), 125.63 (d), 125.66 (d), 125.75 (d), 140.52 (s), 142.26 (s), 142.38 (s), 142.83 (s), 228.61 (s, CO); IR (CDCl$_3$) ν 1715 cm^{-1}; MS (30 eV): m/z (rel. int.) 376 (M$^+$, 20%), 178 (100%); Anal. calcd for $C_{28}H_{24}O$: C 89.32, H 6.42; found: C 88.95, H 6.20. Compound **6** (66% yield): ^{1}H NMR (CDCl$_3$), δ -0.40 (dm, J = 11 Hz, H(12s)), 0.17 (t, J = 5Hz, 1H, cyclopropyl), 0.39 (dm, J = 11 Hz, H(12a)), 0.90 (t, J = 5 Hz, 1H, cyclopropyl), 0.94 (t, J = 5 Hz, 1H, cyclopropyl), 1.26-1.33 (m, 3H), 1.42-1.47 (dt, J = 4 & 11 Hz, 1H), 1.63 (m, 1H), 1.76 (m, 1H), 1.85 (dm, J = 10 Hz, 1H), 1.90 (m, 1H), 1.93 (m, 1H), 1.94-2.00 (m, 1H), 2.09 (d, J = 3 Hz, 1H), 3.92 (s, 1H), 4.14 (d, J = 3 Hz, 1H), 7.05-7.16 (m, 6H), 7.21-7.26 (m, 2H); ^{13}C NMR (CDCl$_3$), δ 15.70 (d, 2C), 15.72 (d), 34.13 (t), 34.84 (d), 35.05 (t), 35.35 (t), 36.65 (d), 41.44 (d), 42.64 (d, 2C), 49.10 (s), 49.78 (d), 49,87 (d), 52.89 (d), 56.02 (d), 122.84 (d), 123.85 (d), 124.03 (d), 124.86 (d), 125.26 (d), 125.70 (d, 2C), 125.96 (d), 143.29 (s), 143.64 (s), 143.71 (s), 144.81 (s).

Cycloaddition of 1 with cyclopentadiene. The olefin **1** (61 mg, 0.31 mmol) was dissolved in toluene (20 mL), and to it was added freshly distilled cyclopentadiene (49 mg, 0.74 mmol). The solution was stirred at room temperature under nitrogen for 6 h, then was heated to reflux for another 1 h. The solvent was evaporated *in vacuo* and the adduct **7** was recrystallized from ether/$CHCl_3$ (60 mg, 0.23 mmol, 74%). ^1H NMR ($CDCl_3$), δ 1.34 (dm, J = 8 Hz, 1H), 1.51 (d, J = 8 Hz, 1H), 1.58 (m, 2H), 1.91-2.00 (m, 2H), 2.12 (dd, J = 7 & 12 Hz, 1H), 2.35-2.81 (m, 10H), 3.12 (qm, J = 8 Hz, 1H), 6.10 (m, 1H), 6.21 (m, 1H); ^{13}C NMR ($CDCl_3$), δ 45.33 (t), 46.61 (d), 48.25 (d), 49.03 (d), 49.88 (t), 50.17 (t), 52.09 (d), 52.84 (d), 53.06 (d), 53.23 (d), 56.13 (d), 56.36 (d), 56.68 (d, 2C), 58.52 (d), 70.14 (s), 134.69 (d), 137.11 (d), 229.51 (s); MS (60 eV): m/z (rel. int.) 264 (M^+, 70%), 246 (20%), 230 (10%), 198 (100%), 179 (10%), 170 (42%), 164 (84%).

Acknowledgement. The authors thank Professor W. S. Tse and N. T. Liang in the Institute of Physics of Academia Sinica for recording the resonance Raman spectra. This work was supported in part by the National Science Council of the Republic of China.

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