SYNTHESIS AND PROPERTIES OF 5-CYCLOHEPTATRIENYLIDENE-2(5H)-THIOPHENONE[1]

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The title compound $\underline{3}$ was prepared in 4 steps starting from 2,5-dibromothiophene in good yield. This synthetic method is advantageous for the easy preparation of the annulenones having an inserted quinonoid ring. The compound $\underline{3}$ is quite stable and proved to have a highly bond-alternated olefinic character on the basis of NMR data and dipole moment.

The cyclic cross-conjugated carbonyl compounds such as $\underline{2}$ (R=H, Br, OMe, tBu, etc.) have been synthetically investigated so far by the several research groups.[2] One of the interests in the chemistry of this type of the compounds is centered around the questions how the extent of electron delocalization in the seven-membered ring will be influenced by introducing a π-conjugated ring system between oxygen atom and the carbon ring of tropone $\underline{1}$. Unfortunately, the ground state properties of $\underline{2}$ have never been fully investigated due to the instability or difficult solubility of these compounds. To get more detailed confirmations on this regard, we have now synthesized the sulfur analog $\underline{3}$ and discussed spectroscopically its electronic structure, which is reported herein.

2-Bromo-5-(cyclohepta-2,4,6-trienyl)thiophene, obtained through the Grignard reaction of the magnesium derivative of 2,5-dibromothiophene with 7-methoxycycloheptatriene, was thermally isomerized by refluxing in xylene for 1.5 hr to give $\underline{4}$ (a pale yellow oil, 89%, δ(CCl$_4$) 6.87 (d, H-3, J=4.0 Hz), 6.71 (d, H-4), cycloheptatrienyl: 6.72, 6.30, 5.40, and 2.28). Grignard reaction of the magnesium derivative of $\underline{4}$ with t-butyl perbenzoate in ether gave $\underline{5}$ (a pale yellow oil, 80%,

δ(CDCl$_3$) 6.71 (d, H-4, J=4.1 Hz), 6.21 (d, H-3), 1.35 (s, tBu)). Treatment of $\underline{5}$ with a trityl salt in dichloromethane at 0 °C, and then with cold water gave crude $\underline{3}$, whose silica-gel chromatography (CH$_2$Cl$_2$-n-hexane = 5:1) and the subsequent recrystallization from dichloromethane-n-hexane led to pure $\underline{3}$ (dark maroon plates, m.p. 90-91 °C, 79%, ν max (KBr) 3040, 1640, 1623, 1549, 1508, 1498
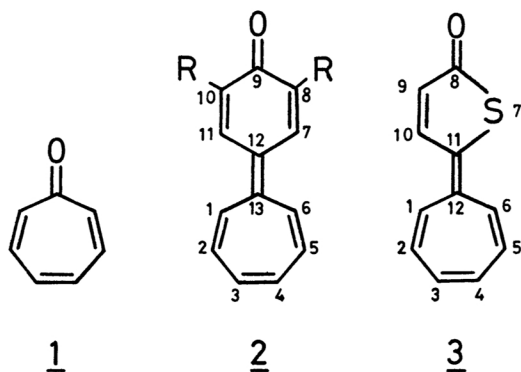
, 1463, 1418, 1318, 1254, 1155, 810, 799, 737 cm^{-1}; λ max (c-hexane) 259 nm (log ε 3.64), 268 (3.64), 427 (4.40); m/e (%) 188 (100) M$^+$, 160 (24) M$^+$-CO, 134 (18) M$^+$-COC$_2$H$_2$, 128 (17) M$^+$-COS, 116 (18) M$^+$-COCS, 115 (43)). Compound 3 is stable at room temperature in solid and in solution, but in trifluoroacetic acid it quantitatively and reversibly turns to its conjugate acid 6 (δ(CF$_3$CO$_2$H) 8.66 (m, H-1,6), 7.80 (m, H-2,3,4,5), 8.20 (d, H-10, J=5.0 Hz), 6.77 (d, H-9); λ max (CF$_3$CO$_2$H) 492 nm (log ε 4.63)). The condensation reaction of 3 with nitrogen bases such as amine, hydroxylamine, hydrazine or with active methylene nucleophiles did not proceed.
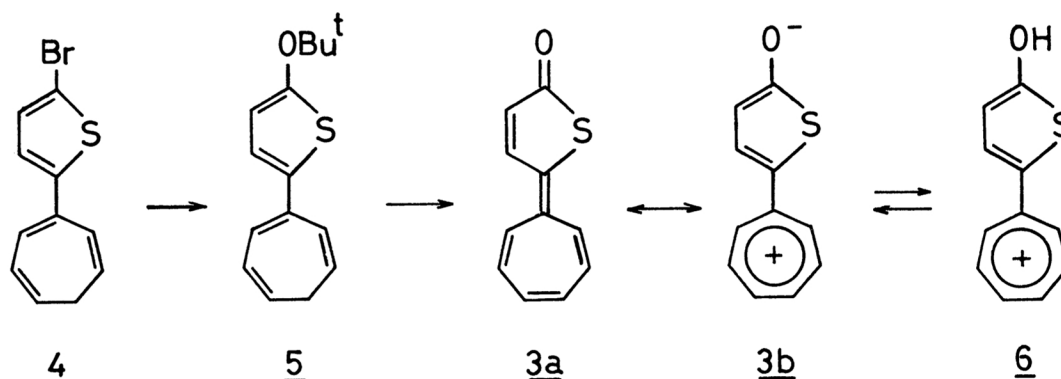
As shown by Table 1, the 1st excitation band of 3, like 2 (R=tBu),[2a] showed a red shift on going from less polar to polar solvents, indicating a larger contribution of the quinonoid structure 3a to the ground state. The ^{1}H-NMR chemical shifts (Table 2) of H-2~H-5 of 3 are found to be 0.99 ppm more upfield than that of H-4,5 of tropone[3] and much the same (by 0.26 ppm upfield in C$_6$D$_6$) as those of sesquifulvalene 7[4] (δ CDCl$_3$ 7.05 (dm, H-1,6), 6.40~6.00 (m, centered at 6.20, H-2 ~ H-5), J$_{1,2}$=J$_{5,6}$=12.0 Hz; δ C$_6$D$_6$ 6.72 (dm, H-1,6), 5.70~5.59 (m, centered at 5.66 , H-2~H-5)). This fact, together with the large vicinal proton coupling constants J$_{1,2}$, J$_{5,6}$, and J$_{9,10}$, and with ^{13}C-NMR chemical shifts of the seven-membered ring carbons, C-2, 3, 4, 5 appeared in the relatively higher field (Table 3), suggests that the compound 3 possesses a highly localized poly-ene system in the ground state. In order to evaluate the contribution extent of 3b to 3, a model compound 8 (colorless plates, m.p. 33-34 °C, 45%, ν max (KBr) 2940, 2860, 1660, 1652, 1590, 1443, 1340, 1150, 1093, 810, 636 cm^{-1}; λ max (c-hexane) 276 nm (log ε 3.83), 326 (4.09); m/e (%) 195 (27) M$^+$+1, 194 (100) M$^+$, 113 (52)) was prepared by the Grignard reaction of 2-t-butoxy-5-thienylmagnesium bromide and cycloheptanone. The IR absorption band of the carbonyl group of 3 appeared at slightly lower frequency region than that of 8, and ^{13}C-NMR chemical shifts (Table 3) of the five-membered ring carbons, C-9, 10, 8, and 11 in 3 appeared at higher field by 2.7, 1.8, 1.8, and 3.3 ppm respectively than those of the corresponding carbons in 8. From these facts the five-membered ring of 3 appears to be a little electron-richer compared with that of 8. The experimental dipole moments of 3 and 8 are also determined to be 5.90 D and 5.16 D respectively. Two models[7] were chosen for the CNDO/2 calculation[8] of dipole moment of 3, model A taken from the X-ray data of tropone[9] and 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene,[10] model B utilizing

Table 1 : Effect of the Solvent Polarity on the 1st Excitation Bands of 3 and 2.[2a] nm (log ε)					
Compd.	DMSO	MeCN	Acetone	c-Hexane	Shift
3	447 (4.42)	437 (4.42)	435 (4.39)	427 (4.40)	+
2 R=tBu	—	467 (4.49)	—	437 (4.50)	+
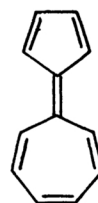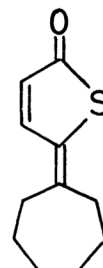
the X-ray data of the same dihydrothiophene as above along with the standard alternating bond lengths[11] and internal bond angles of 128.5 ± 0.5 for the seven-membered ring. Of the two calculated dipole moments 7.06 D (model A) and 6.37 D (model B), the latter value of the model B is in better agreement[12] with the experimental value of 3, suggesting that the diatropic character should be very small in the seven-membered ring of 3. The experimental dipole moment increases by 0.74 D from 8 to 3. This seems ostensibly to be due to the contribution of 3b, but it is not true. The above calculation indicates that this deviation in dipole moments would be mainly attributable to the additivity of the vinyl groups rather than the effect of charge separation. The ground state properties of the unstable mother compound 2 (R=H) are not defined yet due to the lack of physical data, but an increase in electron density of the benzoquinone moiety released from the seven-membered ring of di-t-butyl derivative 2 (R=tBu) would be also small judging from the higher-field NMR chemical shifts of the seven-membered ring protons and the dipole moment[13] (Table 2) being almost comparable value to that of 3.

Table 2 : ^{1}H-NMR Data, IR Data, and Observed Dipole Moments of 3, 8, 2,[2a] and 1.[3]						
Compd.		^{1}H-NMR Data δ ppm J in Hz			IR Data	Dipole Moment
	Solvent	H-1,6	H-2 ~ H-5	H-9	H-10		
3	CDCl$_3$	6.95 ~ 6.70 (6.82)	6.30 ~ 6.00 (6.15)	6.17	7.83 J=6.0	1658, 1650 (CHCl$_3$)	5.90
	C$_6$D$_6$ *	5.93 (H-1) 6.05 (H-6) $J_{1,2}=J_{5,6}=12.0$	5.54 ~ 5.28 (5.40)	5.93	6.87 J=6.0	1640, 1623 (KBr)	
1	CDCl$_3$	7.00 br. s		—		1638 (CHCl$_3$) 1645 (KBr)	4.30
	C$_6$D$_6$	6.93 (H-2,7) $J_{2,3}=J_{6,7}=12.0$	6.55 (H-3,6) 6.39 (H-4,5)	—			
8	CDCl$_3$	2.75 2H t 2.58 2H t 1.90 1.50 8H m		6.26	7.83 J=6.0	1660 br. s (CHCl$_3$) 1660, 1652 (KBr)	5.16
2 R=tBu	CDCl$_3$	7.03	6.24 ~ 6.48 (6.33)	7.33 (H-7, 11)		1584 (KBr)	5.83[13]

* Taken at 200 MHz. Chemical shift assignments of H-1 and H-6 were carried out by referring to the long range coupling between H-10 and H-6.

Table 3 : ^{13}C-NMR Data of $\underline{3}$, $\underline{7}$,[5] $\underline{1}$,[6] and $\underline{8}$.   δ ppm at 25 MHz in CDCl$_3$

Compound	Seven-membered ring				Five-membered ring			C=O
	C-1,6	C-2,3,4,5		C-12	C-9	C-10	C-11	
$\underline{3}$	137.5, 135.0	134.0, 134.0 133.8, 132.1		141.8	126.7	142.9	129.9	194.1
	C-1,6	C-2,5	C-3,4	C-12	C-8,9	C-7,10	C-11	
$\underline{7}$	137.6	133.5	134.6	146.5	129.9	118.6	138.6	—
	C-2,7	C-3,6	C-4,5					
$\underline{1}$	142.1	136.1	134.7	—	—			187.5
	C-1~ C-6			C-12	C-9	C-10	C-11	
$\underline{8}$	37.8, 32.7, 29.7, 29.4 28.4, 27.0			152.9	129.4	144.7	133.2	195.9

References and Notes

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