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1,2: 8,9-Dibenzo-3,10-bisdehydro[14]annulene-5,12-dione

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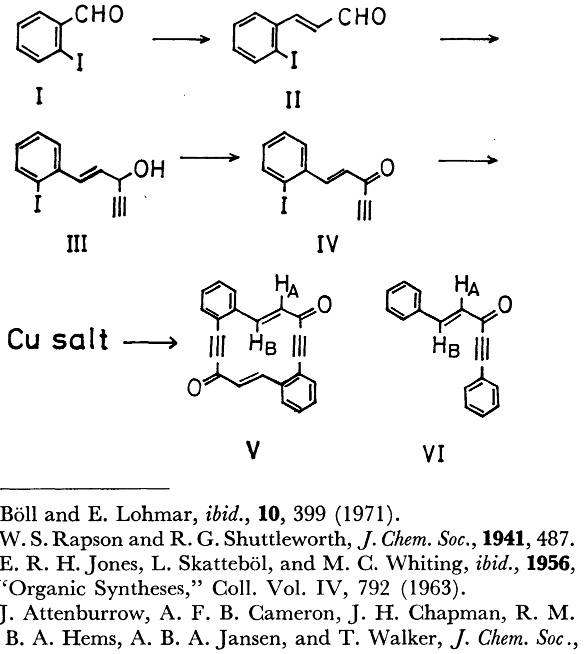
An annelated[14]annulenedione (V) was prepared by the Castro reaction of cuprous salt of *o*-iodocinnamoylacetylene (IV) in order to examine the aromatic character of the inner fourteen membered ring. The NMR spectra of V in arsenic trichloride and deuterotrifluoroacetic acid suggest that significant downfield shift of the inner protons H_B is due to a paramagnetic ring current arising from polarization of two carbonyl groups in the inner ring, compared with the spectra of a reference compound VI.

A series of fully conjugated monocyclic monoketone, so-called annulenone, are predicted to be aromatic or non-aromatic owing to polarization of carbonyl group provided they contain ($4n+3$) membered ring or ($4n+1$) membered ring, respectively. Recently, several annulenones, *e.g.*, 4,9-methano[11],[1] [13],[2a] [15],[2b] and [17][2c] annulenone derivatives, have been synthesized in order to confirm this prediction. On the other hand, as in the case of annulenes, an effect of annelation on aromatic character of annulenone has been explored in a few annelated annulenones, dibenzo-[9],[3] 6,7-benzo-4,9-oxido[11],[4a] 4,7: 10,13-dioxido-[15],[4b] and 2,5: 8,11: 14,17-trioxido[17][4c] annulenones, indicating the delocalization of π-electrons through condensed benzene or furan nuclei.

For the purpose of comparison with the properties of the annelated annulenones, we attempted to examine the effect of annelation on conjugated cyclic diketone or annulenedione.[5] In this paper we wish to report the synthesis and properties of 1,2: 8,9-dibenzo-3,10-bisdehydro[14]annulene-5,12-dione (V). It is expected that this ($4n+2$) membered ring compound is non-aromatic by virtue of polarization of two carbonyl groups and thereby represents a paramagnetic ring current.

Results and Discussion

Synthesis. *o*-Iodocinnamaldehyde (II) was obtained by the reaction of *o*-iodobenzaldehyde with acetaldehyde in anhydrous alcohol at room temperature in 40% yield.[6] The cinnamaldehyde II was treated with ethynyl magnesium bromide[7] in dry tetrahydrofuran to produce an ethynyl carbinol III in a yield of 74%. Oxidation of the carbinol III with active manganese dioxide[8] in carbon tetrachloride at 0°C yielded crude ethynyl *o*-iodostyryl ketone (IV) which gave red cuprous salt in 86% yield by treatment with Ilosvay reagent. Dry cuprous salt of IV was subjected



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to the Castro reaction[9] in anhydrous *N,N*-dimethyl formamide at 120°C to give cyclic dimolecular product, 1,2 : 8,9-dibenzo-3,10-bisdehydro[14]annulene-5,12-dione (V), of fairly thermostable and lemon yellow needles in 1.2% yield. The structure of the annulenedione V was confirmed by elemental analysis and IR, NMR, and Mass spectra. Styryl phenylethynyl ketone (VI) was obtained through the Castro reaction of cuprous salt of cinnamoyl acetylene with iodobenzene as a reference compound for the synthesis and NMR spectrum of V.

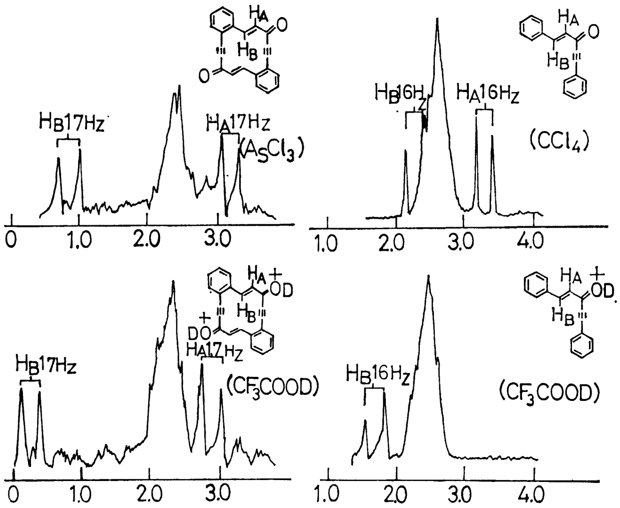


Fig. 1. The NMR spectra of V and VI (60 MHz, TMS)

Table 1. The chemical shifts (τ) of V and VI

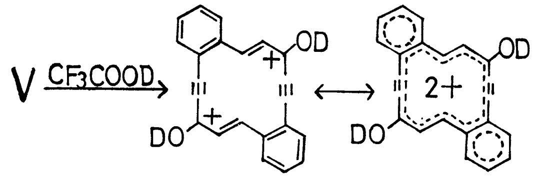
	Solvent	H_B	BzH	H_A
V	$AsCl_3$	0.81	~2.4~	3.14
	CF_3COOD	0.22	~2.3~	2.88
VI	CCl_4	2.27	~2.6~	3.31
	CF_3COOD	1.68	~2.5~	~2.5~

NMR Spectra. The NMR spectra of V and VI are shown in Fig. 1 and Table 1. The spectrum of V was measured in arsenic trichloride and in deuterotrifluoroacetic acid because of poor solubility in the usual organic solvents, while VI gave no distinct spectrum owing to instability in the former medium. The chemical shift of inner protons H_B in V are at considerably lower field ($\Delta\delta$: *ca.* 1.5 ppm) than that of proton H_B in VI, in contrast to somewhat same position of both protons H_A in V and VI. A difference in the chemical shifts in different solvents is *ca.* 0.1 ppm between arsenic trichloride and carbon tetrachloride.[10] The extent to which the shift of the protons H_B in V is affected by shielding effects of the π-electron systems (-C≡C-, -C=C-, and >C=O) and electric field effect of carbonyl group other than a styryl phenylethynyl ketone moiety in V was estimated according to the McConnell equation (1)[11] and the Buckingham equation (2),[12] respectively, to be about −0.7 ppm at most. It is interesting that the protons H_B in V appear

$$\Delta\sigma = \Delta\chi\sum_{i=1}\frac{1}{3R^3}(1-3\cos^2\theta) \tag{1}$$

$$\Delta\sigma = -2\times10^{-12}E_z - 10^{18}E^2 \tag{2}$$

at considerably lower field beyond the combined effect of both effects above-stated. The inner fourteen membered ring of V is considered as a twelve π-electron system, *i.e.*, a 4*n*π ring system of the Hückel rule, through the polarization of two carbonyl groups. So the inner ring system may reveal a paramagnetic ring current and thereby may show downfield shift of the inner protons. Accordingly, the marked downfield shift of the protons H_B in V described above can be accounted for by a total effect of the paramagnetic ring current and the other effects, mainly by the former.



VIIa VIIb

It is expected that when V is protonated, the inner protons H_B may indicate the signal at further lower field by way of additional paramagnetic ring current of the inner ring as depicted by VIIa and VIIb. This prediction was, in fact, realized with the chemical shift in deuterotrifluoroacetic acid as is shown in Table 1 and Fig. 1. In contrast to the chemical shift of the inner proton, the outer protons H_A and the benzenoid protons show little difference in the chemical shift, compared with ones in arsenic trichloride. It is most likely due to internal compensation of the paramagnetic ring current with an effect of positive charge. This postulate is possibly supported by marked down field shifts of both protons H_A and H_B of VI in deuterotrifluoroacetic acid by comparison with the chemical shifts in carbon tetrachloride.

Experimental

All melting points are uncorrected. The electronic, infrared, NMR, and mass spectra were measured on Hitachi ESP-3T, Jasco DS-402G, Hitachi R-20, and Hitachi RMU-7, respectively.

*1-*o*-Iodophenyl-1-penten-4-yn-3-ol (III).* To an ethynylmagnesium bromide[7] solution prepared by introduction of acetylene into ethylmagnesium bromide (from 6.9 g, 0.29 g-atom of magnesium and 30 g, 0.28 mol of ethyl bromide) in dry tetrahydrofuran added dropwise *o*-iodocinnamaldehyde[6] (II, 50 g, 0.19 mol) in dry tetrahydrofuran (100 m*l*) under ice cooling and stirring. After stirring at room temperature overnight, the reaction mixture was poured into a cooled aqueous solution saturated with ammonium chloride to decompose the Grignard complex. The aqueous layer was extracted with ether and the combined organic solution was washed with water and dried over magnesium sulfate.

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[9] R. D. Stephens and C. E. Castro, *ibid.*, **28**, 3313 (1963); C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **31**, 4071 (1966); C. E. Castro, R. Havlin, V. K. Honwad, A. Malte, and S. Mojé, *J. Amer. Chem. Soc.*, **91**, 6464 (1969).

[10] Cf. the protons of benzalacetophenone and dibenzalacetone, which show complicated patterns, in carbon tetrachloride are shifted to higher field by 0.05—0.15 ppm than in arsenic trichloride.

[11] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[12] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

After evaporating organic solvent, the residue (57 g) was subjected to high vacuum distillation to give pale yellow oil (45 g, 83% yield) of the ethynyl carbinol III, bp 135—137°C/3×10^{-2} mmHg.

IR(neat): 3300 (s, ν_{OH}), 3250 (s, $\nu_{\equiv CH}$), 2200 (w, $\delta_{C\equiv C}$),960 (s, $\delta_{trans\ CH=CH}$), and 750 cm^{-1} (s, *o*-substituted benzene). NMR (CCl_4): τ 2.18—3.31 (m, 4H, aromatic), 3.04 (d, J=15 Hz, 1H, olefin), 3.91 (dd, J=5, 15 Hz, 1H, olefin), 4.45 (m, 1H, methine), 6.52 (broad, 1H, OH), 7.45 (d, J=2 Hz, 1H, acetylene). Found: C, 46.29; H, 3.00; I, 45.02. Calcd for $C_{11}H_9OI$: C, 46.49; H, 3.19; I, 44.67.

o-Iodocinnamoylacetylene (IV). A suspension of active manganese dioxide[8] (100 g) in a carbon tetrachloride (500 m*l*) solution of above carbinol III (10 g, 36 mmol) was stirred under ice-cooling for 1.5 hr. After filtration and washing sufficiently with acetone, the combined filtrate and washings were evaporated in vacuum. Dark red residual solid (8.2 g) was used to prepare cuprous salt as it is because of difficult purification. A small amount of crude sample was extracted with ether and recrystallized from petroleum ether to give yellow plates of the ketone IV, mp 70—71°C.

IR (Nujol mull): 3210 (m, $\nu_{\equiv CH}$), 2100 (s, $\nu_{C\equiv C}$), 1630 (s, $\nu_{C=O}$), 979 (m, $\delta_{trans\ CH=CH}$), 765 cm^{-1} (m, *o*-substituted benzene). NMR (CCl_4): τ 1.92 (d, J=16 Hz, 1H, olefin.), 2.16—3.10 (m, 4H, arom.), 3.44 (d, J=16 Hz, 1H, olefin), 6.70 (s, 1H, acetylene). Found: C, 46.95; H, 2.33; I, 44.62. Calcd for $C_{11}H_7OI$: C, 46.83; H, 2.50; I, 44.98.

1,2:8,9-Dibenzo-3,10-bisdehydro[14]annulene-5,12-dione (V). To a solution of Ilosvay's reagent was added a solution of above-stated crude ketone IV (9 g, 31 mmol) in ethanol (100 m*l*) and acetone (50 m*l*) to give immediately red precipitate of cuprous salt. The cuprous salt was filtered, washed with water, ethanol, and ether, successively, and dried in vacuum at room temperature, 9.5 g (86% yield).

Dry cuprous salt (5.0 g, 15 mmol) in dry *N*,*N*-dimethyl formamide (150 ml) was heated with stirring at 120°C under nitrogen for 8 hr. After cooling the reaction mixture was poured into water and extracted with benzene. The organic layer was wahsed with water, dried over magnesium sulfate, and evaporated in vacuum. The residual solid dissolved in benzene was filtered through silica gel with benzene and ether–benzene (1: 99). After evaporating the solvent, crude solid was triturated with benzene and recrystallized from same solvent with active charcoal to give lemon yellow needles of the annulenedione V, mp>500°C, 27 mg (1.2% yield).

IR (Nujol mull): 2200 (s, $\nu_{C\equiv C}$), 1630 (s, $\nu_{C=O}$), 975 (m, $\delta_{trans\ CH=CH}$), 765 cm^{-1} (m, *o*-substituted benzene). UV (THF): λ_{max} (ε), 217 (35400), 304 nm (42200); Mass, *m/e* 308 (M^+). Found: C, 85.74; H, 3.77. Calcd for $C_{22}H_{12}O_2$: C, 85.70; H, 3.92; mol wt 308.

Styryl Phenylethynyl Ketone (VI). Styryl ethynyl carbinol[7] prepared by ethynylation of cinnamaldehyde was oxidized with active manganese dioxide in carbon tetrachloride to give cinnamoyl acetylene. Cuprous salt of this acetylenic ketone was subjected to the Castro reaction with iodobenzene in pyridine to yield a ketone VI, mp 72—73°C (lit,[13] 69—70°C).

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