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HIGHLY POLARIZED TROPONES.
9*H*-AZULENO[1,2,3-*ij*]NAPHTHALEN-9-ONE AND 8*H*-AZULENO[1,2,3-*ij*]NAPHTHALEN-8-ONE

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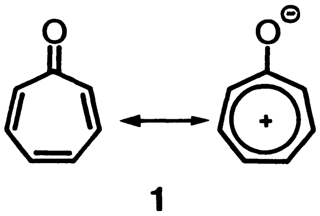
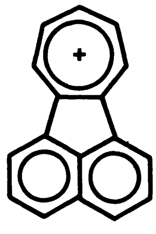
9H-Azuleno[1,2,3-*ij*]naphthalen-9-one (**3a**) and 8H-Azuleno[1,2,3-*ij*]naphthalen-8-one (**3b**), consisting of tropone and acenaphthylene have been synthesized. These ketones were found to be highly polarized and highly basic compounds.

In the early stage of troponoid chemistry, tropone (**1**) has generally been considered to be an aromatic system due to a substantial contribution of the polarized tropylium oxide structure (**1a**) to its ground state, exemplified by its high dipole moment (4.30 D),1) low carbonyl streching frequency (1595 cm^{-1}),2) and high basicity (H_o= -0.60,3) -1.024)). However, a recent study of its physical properties and a theoretical calculation have been argued against the basis for this assumption.5) Thus, from the detailed examination of the dipole moment in conjunction with CNDO/2 calculations and ^{1}H-NMR spectrum, Bertelli *et al.* suggested that the dipolar character of tropone has hitherto been greatly overestimated and the ground state of tropone exhibits a marked bond alternation characteristic of polyenone. This conclusion was also supported by SCF-MO calculations.6)


1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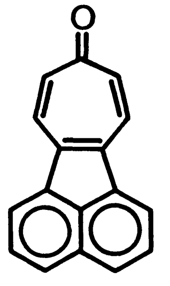
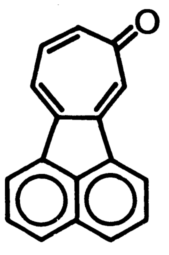
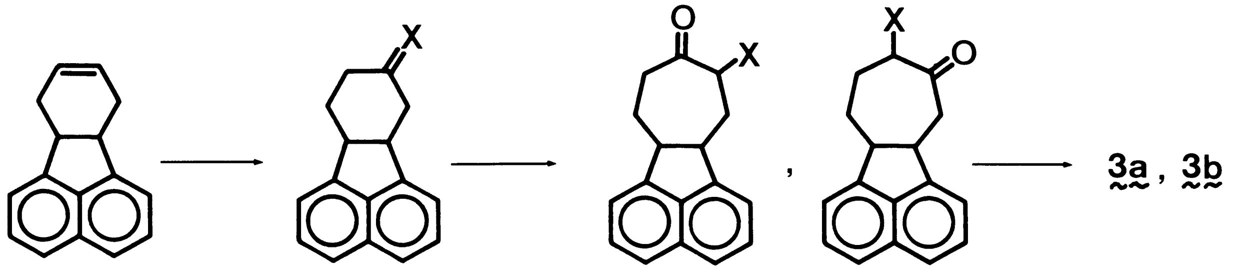

3a


3b

On the other hand, we have already reported that among the many hydrocarbon cations so far synthesized the cyclohept[*a*]acenaphthylenylium ion (**2**) was found to be particularly stable (pK_R+ = 8.7).7) This finding suggests that the corresponding ketones such as 9*H*-azuleno[1,2,3-*ij*]naphthalen-9-one (**3a**) and 8*H*-azuleno[1,2,3-*ij*]naphthalen-8-one (**3b**) were expected to be the highly polarized tropones. We now report the synthesis and some properties of **3a** and **3b**.

The preparation of **3a** and **3b** began with 6b,7,10,10a-tetrahydrofluoranthene (**4**)8) which was synthesized according to a known procedure. Hydroboration of **4** [$NaBH_4$/HOAc/THF/0°C, 100% yield] gave the alcohol **5** which upon oxidation with pyridinium chlorochromate [CH_2Cl_2/r.t./1 h, 76% yield] afforded the ketone **6**,9) colorless needles, mp 111°C, $\nu_{C=O}$ 1700 cm^{-1}. Ring expansion of **6** was carried out via the diazo-ester **7**9) [$N_2CHCOOC_2H_5$/ether-THF(1:1)/*n*-BuLi/-110°C,10) 60% yield, yellow oil, ν_{N_2} 2090 cm^{-1}] which was treated with a catalytic amount of π-allylpalladium chloride dimer in chloroform [-60°C then allowed to warm to r.t./10 h] to give a mixture of the keto esters, 8a and 8b, $\nu_{C=O}$ 1700, 1730 cm^{-1}, in quantitative yield. Acid hydrolysis followed by decarboxylation of the mixture [HOAc/HCl/ reflux/6 h] afforded a 1:6 mixture of the cycloheptanones, 9a[9] and 9b,[9] whose separation was accomplished by a medium pressure column chromatography. The distinction between 9a, colorless needles, mp 123-124°C, $\nu_{C=O}$ 1692 cm^{-1}, and 9b, colorless needles, mp 94-95°C, $\nu_{C=O}$ 1696 cm^{-1}, was easily made through ^{13}C-NMR spectral comparison in which 9b showed six sp^3-C signals at δ 34.08, 40.64, 53.84, 54.88, 56.48, and 58.49 whereas 9a exhibited only three signals at δ 37.33, 57.23, and 57.76 in the region of sp^3-C compatible with the C_{2v} symmetric structure. Final dehydrogenation of 9a and 9b with DDQ [benzene/reflux/4 h] gave the symmetric tropone (3a),[9] deep red plates, mp 149-150°C, MS m/e 230 (M^+, 24%), 202 (M^+-CO, 100%), and the unsymmetric tropone (3b),[9] reddish orange plates, mp 205°C, MS m/e 230 (M^+, 14%), 202 (M^+-CO, 100%), respectively.



4

5 : X = <H, OH

6 : X = O

7 : X = <OH, CN_2CO_2Et

8a : $X = CO_2Et$ 8b

9a : X = H 9b

The electronic spectra of 3a and 3b in methanol (Figure 1a)[11] showed quite different absorption patterns whereas those in 96% sulfuric acid (Figure 1b)[11] indicated the four principal absorption bands similar to those of the parent ion 2[7] in the similar regions attributable to the formation of the corresponding hydroxytropylium ions.

The infrared spectra of 3a and 3b are shown in Figures 2a and 2b, respectively. As can be seen from the Figures, the characteristic bands for the carbonyl groups of 3a and 3b appear at 1580 and 1550 cm^{-1}, respectively. These values are substantially lower than that of the parent tropone (1) clearly indicating the highly polarized nature of 3a and 3b.[12]

An alternative measure of polarity of ketones would be the basicity. The tropones 3a and 3b were protonated reversibly in conc. sulfuric acid. Quantitative evaluation of the basicity of tropones is usually made by determination of H_o[13] of a solution in which the tropone is half-protonated. This is most conveniently done spectrophotometrically in a mixture of dioxane and aqueous perchloric acid from which half-protonation occurs at $H_o = +1.2 \pm 0.05$ for 3a and $+1.1 \pm 0.1$ for 3b. Thus, 3a and 3b are about hundred times more basic than the parent tropone. The high basicities of 3a and 3b may be attributed to the high thermodynamic stability

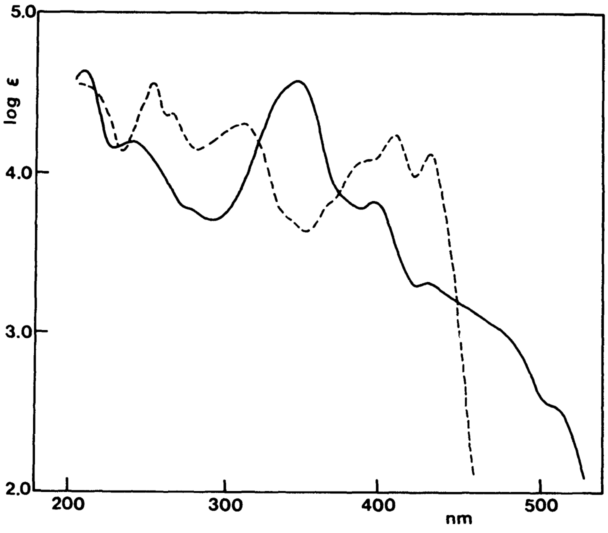


Figure 1a.

Electronic spectra of 3a (——) and 3b (– – –) in CH$_3$OH.

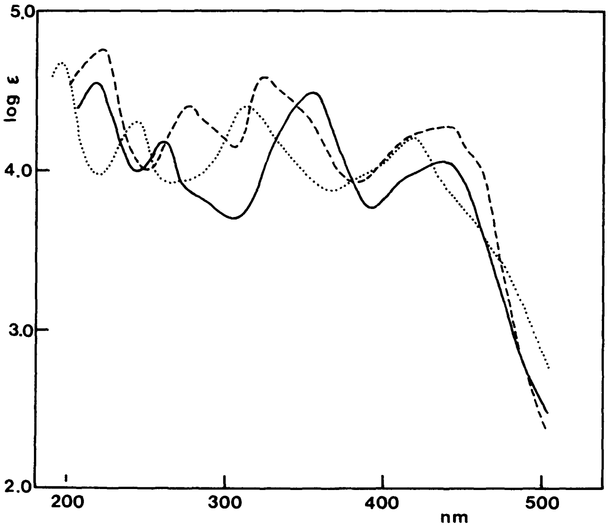


Figure 1b.

Electronic spectra of 3a (——), 3b (– – –), and 2 (⋯⋯) in 96% H$_2$SO$_4$

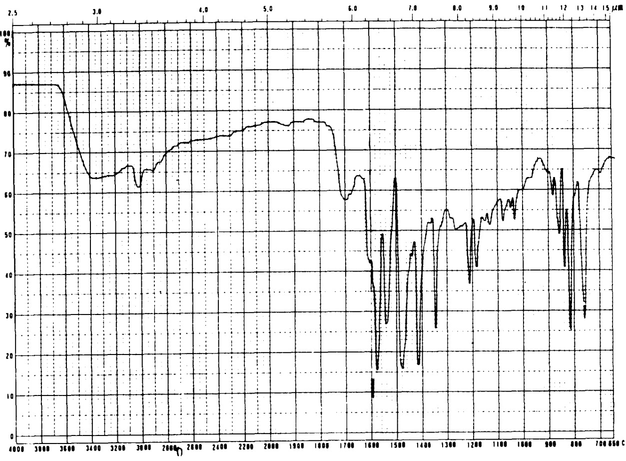


Figure 2a.

Infrared spectra of 3a (KBr).

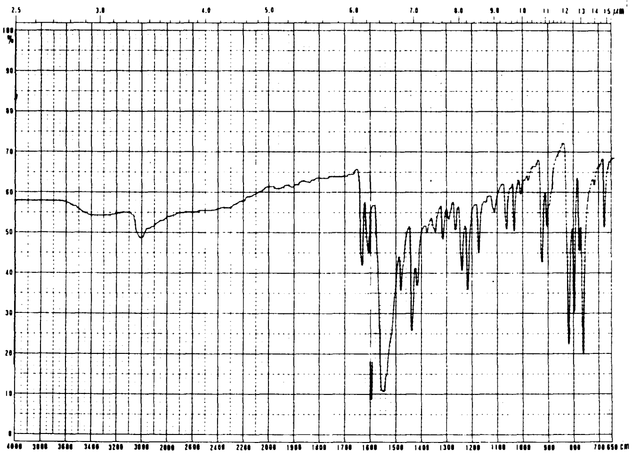


Figure 2b.

Infrared spectra of 3b (KBr).

of the cyclohept[*a*]acenaphthylenylium ion (**2**).

To the best of our knowledge the tropones **3a** and **3b** are most basic ketones so far known. Finally, it should be noted that **3a** has a skeletal structure of grandirubrine, a novel tropoloisoquinoline alkaloid.[14)]

References

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11) **3a**: λ_{max} (CH_3OH) 209 nm (log ε 4.64), 235(sh, 4.28), 241(4.30), 344(4.60), 394 (3.86), 429(3.33), 452(sh, 3.17), 477(sh, 3.03); λ_{max} (96% H_2SO_4) 218(4.55), 261(4.18), 355(4.49), 414(sh, 3.95), 436(4.06).
3b: λ_{max} (CH_3OH) 210(4.55), 254(4.57), 264(4.37), 286(sh, 4.18), 307(4.33), 385(4.09), 404(4.23), 428(4.14); λ_{max} (96% H_2SO_4) 221(4.77), 275(4.41), 297 (sh, 4.24), 332(4.60), 416(4.23), 443(4.29).
12) ^{1}H-NMR spectra of **3a**, δ ($CDCl_3$) 7.19 and 8.04 (AA'BB', 4H, H-7,8,10,11), 7.56-8.00 (m, 6H), and **3b**, δ ($CDCl_3$) 7.1-7.3 (m, 2H), 7.5-8.0 (m, 8H) do not provide any useful information concerning the polarity of these compounds.
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