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5-CYCLOHEPTATRIENYLIDENE-2(5H)-FURANONE
CHARACTERIZATION OF A FURAN-INSERTED TYPE COMPOUND OF TROPONE 1)

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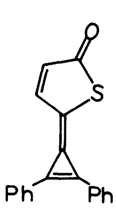
The title compound, a new inserted type tropone, has been prepared. This planar compound showed an unexpectedly small contribution of the dipolar structure to the ground state, as compared with parent tropone, suggesting a general trend that the net conjugative electronic interaction between a cycloheptatrienylidene group and an electronegative oxygen atom is slight. The slight conjugative interaction was evidenced by a weak electronic spectral E_1 band having a C-T character.

Our interest has been focused in recent years on an inserted type annulenone, *i.e.* a compound in which a conjugative π-system is inserted between the oxygen atom and the carbon ring of the parent annulenone. We have synthesized previously thiophene-inserted type annulenones 1 3) and 2, 4) and found that the diatropic character of the terminal ring is unexpectedly weakened in 2 whereas is not virtually weakened in 1 as compared with parent tropone and diphenylcyclopropenone, respectively. Such a difference in insertion effect between 1 and 2 would be mainly attributable to a) the difference in electronic conjugative interaction between the oxygen atom and cyclopropenylidene or cycloheptatrienylidene group through the inserted heterocyclic ring (electronic factor) and/or b) the difference in the coplanarity of the molecules 1 and 2 (geometric factor). Whereas 1 exists possibly in a coplanar conformation, 2 may exist in a non-planar one because of the nonbonded atom interactions between the ortho hydrogen atoms H-1 and H-10 (1.88 Å) and between the sulfur atom and H-6 (2.35 Å). 5,6) Therefore the electronic structural study on an inserted type tropone, having a planar conformation, becomes necessary in order to know which of the two factors mentioned above is really responsible. One of the desirable compounds on this account is a furan-inserted type tropone 3 7) in which such non-bonded atom interactions are more alleviated because the distances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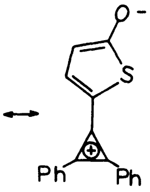
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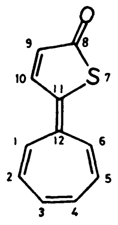

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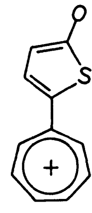
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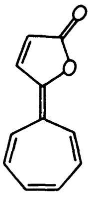
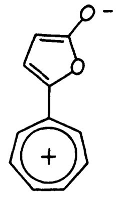
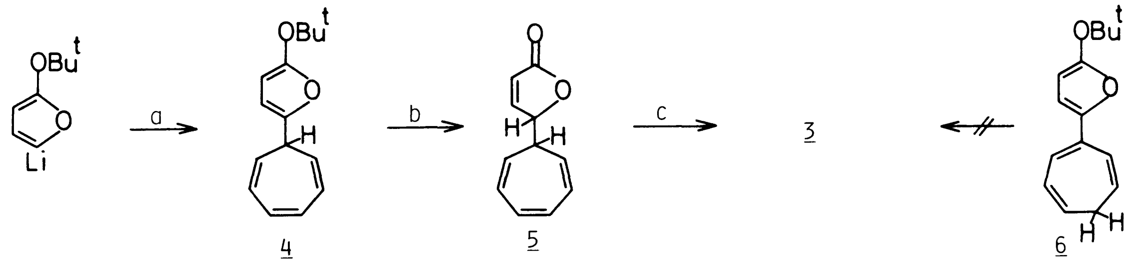

3a


3b

of non-bonded atoms H-1 ∼ H-10 and of oxygen-7 ∼ H-6 are estimated to be 2.1 and 2.35 Å, respectively, on the idealized model [3] constructed utilizing the X-ray data of strigol for the furan ring and standard bond lengths and internal angles of 128.5 ± 0.5° for the seven-membered ring. In this communication compound 3 has been synthesized and its electronic structure has been investigated, suggesting that the electronic factor rather than the geometric factor plays an important role in a characterization of the ground states of these inserted type annulenones.

The synthesis of 3 was carried out according to the route shown in the Scheme. 2-t-Butoxyfuranlithium[8] was first allowed to react with tropylium fluoroborate[9] to give 4 [pale yellow oil, MS m/e (%) 230 (1, M^+), 174 (63), 129 (100), yield 80%]. Reaction of 4 with p-toluenesulfonic acid led to the furanone 5 [yellow needles, mp 58-59 °C, MS m/e (%) 174 (0.5, M^+), 172 (0.5), 144 (1), 91 (100); IR (KBr) 1735 cm^{-1}, yield 90%]. Oxidation of 5 with DDQ yielded the desired 3 in 15% yield together with a fairly high recovery (50-60%).[10] An alternate path involving hydride abstraction of 6 followed by the neutralization of the resulting de-t-butylated cycloheptatrienium ion was unsuccessful. Compound 3[11] is stable to air at room temperature, or even at higher temperatures (up to around 100 °C) in a short period, and its structure is confirmed by the following spectroscopic data and elemental analyses [3: mp 92-93 °C, MS m/e (%) 172 (100, M^+), 144 (15), 115 (52), 90 (57): IR (KBr) 1725, 1564, 1504, 1257 cm^{-1}; Electronic spectrum (cyclohexane) λmax 249 nm (log ε 3.73), 407 (4.46), 428 sh (4.32), 510 sh (2.73); ^{1}H NMR (Table); ^{13}C NMR (Fig. 2)].

Scheme



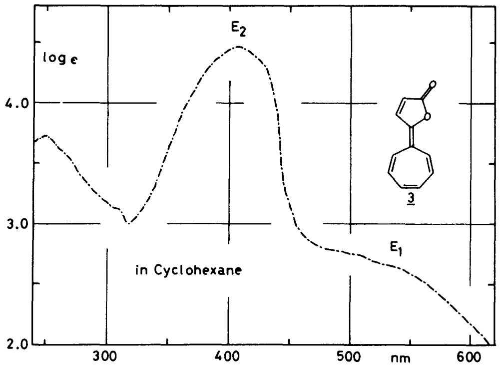
a) tropylium fluoroborate (0.8 equiv.) in ether, 0 °C (1 h).
b) p-TsOH (cat. amount) in benzene, 40 °C (2 h).
c) DDQ (1.0 equiv.) in dioxane, 60 °C (2 h).

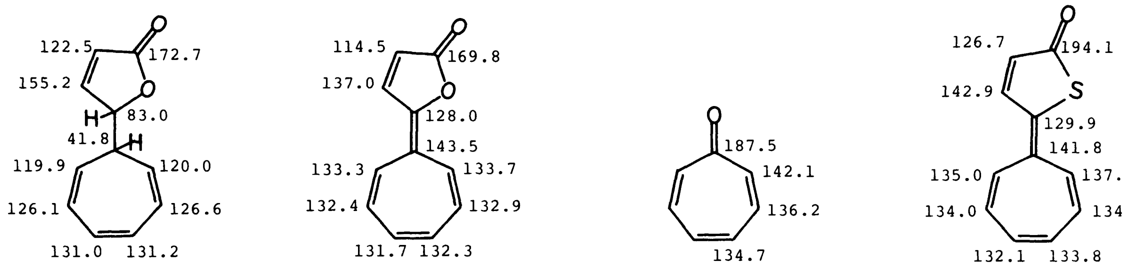
^{1}H NMR chemical shift of H-9 of 3 is about 0.22 ppm upfield from the corresponding proton of 5. ^{13}C NMR chemical shifts of C-8 and C-9 of 3 are 2.9 and 8.0 ppm upfield from those of 5, respectively, whereas the seven-membered ring carbons C-3,4 of 3 are about 1∼2 ppm downfield from those of 5. The IR spectral carbonyl band of 3 appeared at about 10 cm^{-1} lower frequency region than that of 5. ^{1}H NMR vicinal coupling constant *J*9,10 of 3 is 0.3 Hz smaller than that of 5.

Table : ^{1}H NMR data of 3, 2, 5, and tropone, δ ppm, *J* in Hz

Compd.	Solvent	H-1,6	H-2 ∼ H-5	H-9	H-10
3	$CDCl_3$	6.72 (H-6) 6.41 (H-1)	5.98-6.10 (6.04)	5.99	7.55
	C_6D_6	6.49 (H-6) 5.66 (H-1)	5.24-5.48 (5.36)	5.53	6.55
		*J*1,2=*J*5,6=12∼12.5, *J*1,6=2.0		*J*9,10=5.5	
2	$CDCl_3$	6.70-6.95 (6.82)	6.00-6.30 (6.15)	6.17	7.83
5	$CDCl_3$	2.16 (dt, H-11), 5.20 (m, H-1,6) 6.30 (m, H-2,5), 6.66 (m, H-3,4)		6.21 *J*9,10=5.8	7.54
tropone	$CDCl_3$	7.0 br. s		—	—

Fig. 1 Electronic spectrum of 3





5 3 2

Fig. 2 ^{13}C NMR data of 3, 5, 2, and tropone, δ ppm in $CDCl_3$
The assignments of the 7-membered ring carbons are interchangeable.

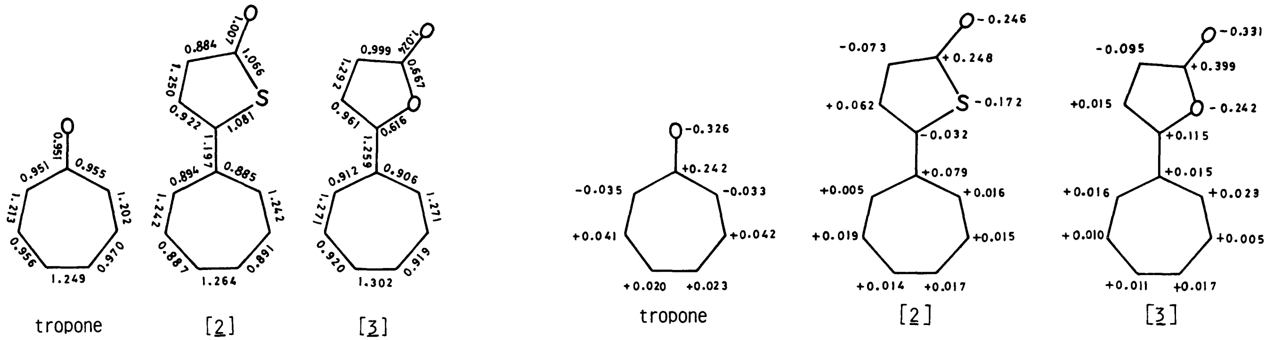
These facts indicate that the dipolar structure 3b contributes to the ground state of 3. The following evidence, however, shows also that the contribution extent of 3b to 3 is only very slight. The electronic spectral 2nd excitation band (E_2) of 3 (Fig. 1)[12] showed a red shift by 14 nm on changing the solvent from less polar cyclohexane [407 nm (log ε 4.46)] to more polar DMSO [421 nm (log ε 4.46)]. The chemical shifts of seven-membered ring protons (H-2,3,4,5) and carbons (C-2,3,4,5) of 3 are about 1 and 3 ppm upfield from those of the corresponding protons and carbons of tropone, respectively. Furthermore, the signals due to the seven-membered ring protons (H-2,3,4,5) and carbons (C-2,3,4,5) of 3 are found at about 0.11 and 1.13 ppm (on an average) higher field than those of the corresponding protons and carbons of 2, respectively. The experimental dipole moment of 3 is found to be 5.56 D, which is 0.34 D smaller than that of 2.

Thus the contribution extent of 3b to 3 is lower than that of 2b to 2, whereas 3 is more planar than 2, demonstrating that the electronic factor rather than the geometric factor is essential for induction of the charge separation in these inserted type annulenones. Theoretical informations obtained from a series of CNDO/2 calculations on tropone[13] and planar models of [3] and [2][5,14] are also consistent with this idea, because the highly localized olefinic characters of 2 and 3 compared with tropone are well reproduced in the calculated bond orders, charge densities, and dipole moments as seen in Fig. 3.

Tropone has been recognized to be more olefinic than diphenylcyclopropenone. On comparing 1 with 2 and 3, it becomes evident that the difference between diphenylcyclopropenone and tropone in olefinic character, *i.e.*, in the extent of electron delocalization, is significantly enlarged upon the insertion of a heterocyclic ring. Inductive effect would not play an important role for the charge separation in these inserted type annulenones because the oxygen atom and the terminal ring are far apart. Therefore, it would be a general trend that a cycloheptatrienylidene group has a poor ability to get into conjugative interaction with an electronegative oxygen atom, in contrast with a cyclopropenylidene group.

Concurrently, the conjugative interaction in 3 should not be disregarded even though slight. The weak electronic spectral E_1 band of 3 (Fig. 1) is considered to be originated from the slight conjugative interaction. The band exhibits a negative tail in the MCD spectrum and is assigned to a $\pi_7 \rightarrow \pi_9^*$ (not to $n \rightarrow \pi^*$) transition according to the CNDO/S method. More interestingly, it is assigned to an absorption having a C-T character due to the electronic transition from the HOMO of the furanone (a donor) to one of the degenerate LUMO's of tropylium ion (an acceptor).[15]

Fig. 3. Bond orders, charge densities, and dipole moments (D) of tropone, [2], and [3] calculated by the CNDO/2 method.



	tropone	[2]	[3]
μ calcd.	4.68	6.37	5.60
μ exptl.	4.30	5.90	5.56

References

1) Cyclic Cross-conjugated Hydrocarbons having an Inserted p-Quinonoid Ring XIII. Part XII: K. Takahashi, K. Nishijima, K. Takase, and S. Katagiri, Tetrahedron Lett., Submitted for publication. Part XI: K. Takahashi et al., Chem. Lett., 1982, 875.

2) S. Katagiri: Department of Chemistry, Hirosaki University, Hirosaki, 036.

3) See Part XII of this series.

4) K. Takahashi, T. Sakae, and K. Takase, Chem. Lett., 1980, 179.

5) The non-bonded atomic distances were estimated on the idealized model [2] constructed from the X-ray data of 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene for the five-membered ring and standard alternating bond lengths for the seven-membered ring.

6) The sum of van der Waals radii of two atoms: H⋯H, 2.0; H⋯S, 2.75; H⋯O, 2.4 Å.

7) The responsibility of these two factors would be difficult to distinguish even in an acyclic π-rope-inserted type tropone, because of obscurity in the coplanarity and s-transoid conformation of the two terminal groups.

8) G. A. Kraus and H. Sugimoto, J. Chem. Soc., Chem. Commun., 1978, 30.

9) To a stirred solution of 2-t-butoxyfuranlithium in ether was added tropylium fluoroborate. An inverse addition of the reagents or operations using other sources of cycloheptatrienylation gave no desired product.

10) The reaction using a more amount of DDQ at higher temperatures resulted in lowering the yield of 3 as well as the recovery of 5.

11) Compound 3, an γ-alkylidenebutenolide, is of interest regarding biological activity and its animal health screening test is in progress.

12) E_2 band of 3 is assigned to the $\pi_7 \rightarrow \pi_8^*$ electronic transition.

13) The CNDO/2 calculations on tropone were carried out by using X-ray geometry.

14) The input geometries would be appropriate because the calculated dipole moments are in satisfactory agreement with the experimental values. [2]: including d orbitals.

15) Detailed discussion will be given in our separate paper: A. Tajiri, M. Hatano, and K. Takahashi, to be published.

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