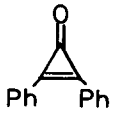
Tetrahedron Letters,Vol.24,No.2,pp 205-208,1983
Printed in Great Britain
0040-4039/83/020205-04$03.00/0

5-(2,3-DIPHENYLCYCLOPROPENYLIDENE)-2(5H)-THIOPHENONE
CHARACTERIZATION OF A THIOPHENE-INSERTED TYPE COMPOUND OF DIPHENYLCYCLOPROPENONE1)

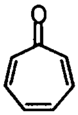
Kazuko Takahashi,* Kazumi Nishijima, Kahei Takase, and Shigeyoshi Katagiri2)
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Summary: The title compound 6 has been synthesized and the effect of cyclic π-system insertion into diphenylcyclopropenone 1 has been discussed. The distribution of positive charge over the 3-membd. ring and phenyl groups slightly predominates in 6 than in parent annulenone 1, in contrast to 5-cycloheptatrienylidene-2(5H)-thiophenone 5 whose 7-membd. ring is more olefinic than parent tropone 2. Electronic spectrum of 6 exhibits a broad absorption band having a C-T character.

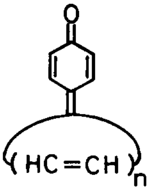
Although the chemistry of annulenones 1, 2, and others has markedly developed,3) the inserted type annulenones, *i.e.* the annulenones in which a conjugative π-system is inserted between the oxygen atom and the carbon ring, have never been fully investigated. The inserted type annulenones such as 3 and 4 are too unstable to be isolated and their physical data except electronic spectra have not yet been known so far, whereas they have been investigated by many research groups.4) We have recently synthesized a stable inserted type tropone 5, and proved that it has a high polyolefinic character in the ground state.5) As the first detailed investigation on the effect of insertion into cyclopropenone system, which is of continuing great interest owing to its unique properties,6) we now describe herein the synthesis of compound 6 and its electronic structural properties obviously different from those of 5.



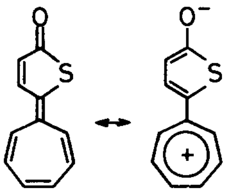
1



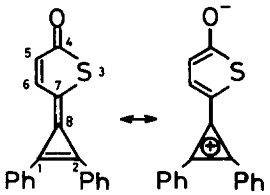
2



3 : n = 1
4 : n = 3



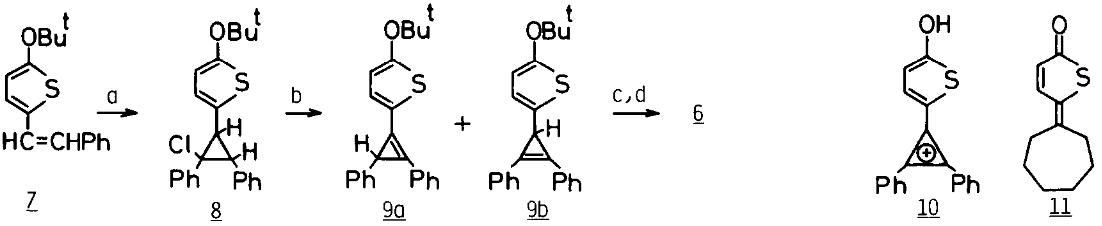
5a
5
5b



6a
6
6b

The synthesis of 6 was achieved *via* the route depicted in the Scheme. Styryl derivative 7 [yellow orange plates, mp 80-82 °C, 93%, trans : cis = 2.7 : 1], obtained by the Wittig condensation of the corresponding formyl derivative,7) was transformed into cyclopropane 8 [yellowish brown needles, mp 78-82 °C, 44%] by the addition of phenylchlorocarbene and thence into a key intermediate 9 [9a: yellow oil, 9b: yellow needles, mp 81-82 °C, 9a : 9b = 1 : 1.5, 92%] by the subsequent dehydrochlorination. The desired compound 6 was obtained in 54% yield by hydride abstraction of 9, followed by neutralization of the resulting de-t-butylated cyclopropenium ion. The compound 6, red needles, mp 164-166 °C, is quite stable in solid state and in solution in contrast to the unstable diphenyl derivative of 3.4a) The structure of 6 is elucidated by the elemental analysis and the following spectral data [6: MS m/e (%) 288 (100, M^+), 260 (16, M^+-CO); IR (KBr) 1852, 1635, 1540 cm^{-1}; ^1H NMR (Table 2); Electronic spectrum (cyclohexane) λmax (log ε) 275 nm (4.35), 352 (3.89), 379 (4.41), 403 (4.06), 474 (3.58)].

Scheme



a: chlorophenyldiazirine (3.0 equiv.) in benzene, reflux (3 h).
b: t-BuOK (1.2 equiv.) in THF, r.t. (1 h), then reflux (30 min).
c: Ph_3CBF_4 (1.1 equiv.) in CH_2Cl_2, 25 °C. d: sat. aq. $NaHCO_3$.

Electronic spectrum of 6 exhibited a characteristic broad absorption band at 420-600 nm (Fig. 1) together with the bands at 370-410 nm which could be resolved into separate components. The resolved absorption maxima and the solvent effect on them are given in Table 1. The broad A-band showed a substantial blue shift on changing the solvent from non polar to polar. Although this kind of solvent effect may correspond to an $n-\pi^*$ type electron transition, this A-band is much more intense (log $\varepsilon \simeq 3.5$) than that of ordinary $n-\pi^*$ transitions, and the reference compound 11 showed no such broad band in a long wavelength region. Therefore, the A-band of 6 is probably assignable to the lowest $\pi-\pi^*$ transition in which electronic interaction along the long molecular axis of 6 could be involved. Moreover, the A-band exhibits a negative tail in the MCD spectrum and is indeed assigned to the lowest $\pi-\pi^*$ electronic transition by the CNDO/S calculations.[8] The A-band is originated from the electronic transition from the HOMO which has appreciably large $2p\pi$AO on C_5 and C_7, and is characteristic of the thiophenone chromophore, to the LUMO which has $2p\pi$AO only on C_1, C_2, and phenyl groups, and comes from the one of the degenerate LUMO's of diphenylcyclopropenium ion. It is of interest to note that the A-band has such an intramolecular C-T character. Absorption bands B and C also showed a blue shift with increasing solvent polarity indicating a larger contribution of the dipolar structure 6b to the ground state resonance hybrid than to the excited state.

Table 1. Effect of the Solvent Polarity on the Electronic Spectral Bands of 3. nm (logε)

Solvent	C-band	B-band	A-band
c-C_6H_{12}	379 (4.41)	403 (4.06)	474 (3.58)
C_6H_6	378 (4.24)	400 (4.28)	460 (3.58)
CH_2Cl_2	372 (4.12)	399 (4.07)	430 (3.44)
Me_2CO	370 (4.13)	395 (4.40)	420 (3.70)
MeCN	370 (4.01)	395 (4.35)	414 (3.84)
$\Delta\lambda$ nm	-9	-8	-60

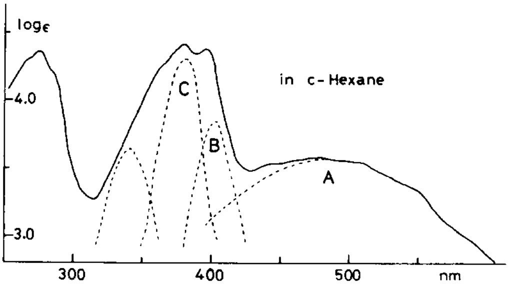


Fig. 1. Electronic spectrum of 6

Table 2. ^{1}H NMR Spectral Data and Dipole Moments of 1, 6, 9b, 10, and 11.

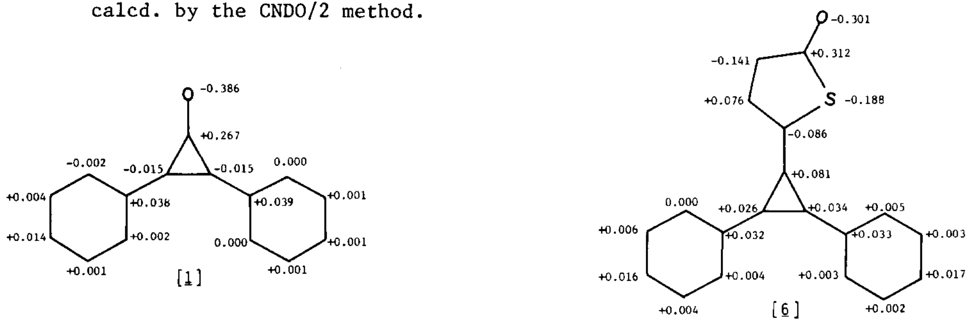
Compd.	^{1}H NMR (100 MHz δ in ppm, J in Hz)								Dipole moment μexptl.
	Solvent	5-Membd. ring protons			Phenyl ring protons				
		H-5	H-6	J5,6	ortho	meta,para	$\Delta\delta$ortho	$\Delta\delta$meta,para	
1	$CDCl_3$	——	——	——	7.90	7.54	-0.16	-0.11	5.08
6	$CDCl_3$	6.15	7.97	5.3	8.06	7.65	0	0	8.94
9b	$CDCl_3$	6.15	6.50	3.8	7.70	7.38	-0.36	-0.27	——
10	CF_3CO_2H	6.91	8.39	4.5	8.35	7.90	+0.29	+0.25	——
11	$CDCl_3$	(H-9) 6.26	(H-10) 7.83	(J9,10) 6.0	——	——	——	——	5.16

^{1}H NMR spectrum of 6 (Table 2) provided a further information in harmony with the above consideration. The vicinal coupling constant J5,6 of 6 is just intermediate between the corresponding ones of the conjugate acid 10$^{9)}$ and the reference compound 11. The ortho and meta-para phenyl proton signals of 6 are found at lower field by 0.36 and 0.27 ppm than the corresponding signals of 9b, respectively, although they are found at higher field by 0.29 and 0.25 ppm than those of 10, respectively.

The phenyl proton signals of 6 are found at nearly the same low field as or at slightly lower field than those of parent compound 1, in contrast to 5 whose signals due to the seven-membered ring protons are found about 1.0 ppm upfield$^{5)}$ from those of 2. The ^{13}C NMR chemical shifts of phenyl groups of 6 are about 0.6-1.0 ppm downfield from those of 1. These data together with the following inspection of the dipole moments and the calculated charge densities lead to an important finding that an extention of the π-conjugation by thiophene-insertion into cyclopropenone 1 brings about no weakening virtually the conjugative interaction between the two terminal groups of system 6, while the conjugative extention by the thiophene-insertion into tropone 2 results in a highly polyenic system 5. The experimental dipole moment of 6 is found to be 8.94 D, which is 3.86 D and 3.78 D larger than those of 1 and 11, respectively, whereas the dipole moment of 5 (5.90 D) is only 1.6 D and 0.74 D larger than those of 2 and 11, respectively. The CNDO/2 calculations on the idealized models [1] and [6]$^{10)}$ yielded dipole moments of 5.13 D for [1] and 9.14 D for [6], both of which are in satisfactory agreement with the experimental values. On the calculated charge densities, given in Fig. 2, we see that the positive charge densities on olefin portion of the three-membered ring and on phenyl groups are slightly greater in [6] than in [1], suggesting that the positive charge is spread over the three-membered ring and the phenyl groups in 6 while the charge separation in 1 is mainly localized on the C=O portion.$^{13)}$

Of the conjugative and inductive electronic interactions between the C=O unit and the πMO's of the olefin portion in annulenones such as 1 and 2, the latter interaction falls off rapidly with increase in the distance of the olefin portion from the carbonyl group whereas the former interaction is not so affected. ^{1}H NMR chemical shifts of phenyl groups of 6 are 0.5-0.4 ppm more downfield than those of tetraphenyltriafulvene.$^{14)}$ Therefore, the difference in the electronic structure between 6 and 5 could be interpreted in part by the fact that the tendency of the respective parent annulenone to exhibit conjugative stabilization interaction, a net π charge

Fig. 2. Charge densities of [1] and [6] calcd. by the CNDO/2 method.



transfer interaction, is pronounced in 1 and less pronounced in 2. Such consideration is in good accordance with the idea derived from the theoretical and photoelectron spectral studies on 1 and 2.15)

References and Notes

1) Cyclic Cross-conjugated Hydrocarbons having an Inserted p-Quinonoid Ring XII. Part XI: K. Takahashi, K. Nishijima, K. Takase, and T. Shimozawa, Chem. Lett., 1982, 875.

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

3) a) F. Pietra, Chem. Rev., 73, 293 (1973); b) F. Sondheimer, Accounts Chem. Res., 5, 81 (1972); c) K. T. Potts, J. S. Baum, Chem. Rev., 74, 189 (1974); d) Z. Yoshida, Top. Curr. Chem., 40, 47 (1973); e) I. Murata, "Riron Yuki Kagaku, Kozo-hen," Kagaku-dojin, 1974, p 191.

4) a) A. S. Kende, J. Am. Chem. Soc., 85, 1882 (1963); b) C. Jutz and F. Voithenleithner, Chem. Ber., 97, 29 (1964); c) P. Bladon, P. L. Pauson, G. R. Procter, and W. J. Rodger, J. Chem. Soc., C, 926 (1966); d) T. Nozoe, Japanese Patent, 17674 (1964); Chem Abstr., 62, 5234.

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

6) a) R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, J. Am. Chem. Soc., 95, 2772 (1973); b) C. U. Pittman, Jr., A. Kress, T. B. Patterson, P. Walton, and L. D. Kispert, J. Org. Chem., 39, 373 (1974).

7) 2-t-Butoxy-5-formylthiophene [brown oil, δ_{CDCl_3} 9.63 (CHO), 7.47 and 6.43 (two d's, J = 4.0 Hz), 1.47 (t-Bu); $\nu_{C=O}$ (neat) 1660 cm^{-1}] was prepared starting from 2,5-dibromothiophene by successive Grignard reactions first with t-butylperbenzoate (75% yield) and then with DMF (50% yield).

8) Detailed characterization of the A-band will be given in our separate paper: A. Tajiri, M. Hatano, and K. Takahashi, to be published.

9) The conjugate acid 10 was obtained by protonation of 6 with CF_3CO_2H.

10) The model [1] is constructed from the average X-ray atomic coordinates of two kinds of molecular structures of 1.11) The model [6] is constructed from the X-ray parameters of 1 described above and 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene.12)

11) H. L. Ammon, J. Am. Chem. Soc., 95, 7093 (1973).

12) B. Aurivillius, Acta Chem. Scand., 26, 3621 (1972).

13) The large negative charge on the carbonyl oxygen in [6] is balanced by a sizable +0.312 positive charge at C_4. But the positive charge on C_4 appears not to affect directly on the three-membered ring because they are far from each other.

14) K. Komatsu, T. Moriyama, T. Nishiyama, K. Okamoto, Tetrahedron, 37, 721 (1981).

15) a) W. Schafer and A. Schweig, Tetrahedron Lett., 1974, 1213; b) C. Muller, A. Schweig, and H. Vermer, J. Am. Chem. Soc., 97, 982 (1975); c) W. R. Harshbarger, N. A. Kuebler, and M. B. Robin, J. Chem. Phys., 60, 345 (1974).

(Received in Japan 4 September 1982)