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SYNTHESIS AND PROPERTIES OF A SERIES OF 1,2,3,4-TETRAHYDRO-1,4-ETHYLIDENEBENZOTROPYLIUM SALTS

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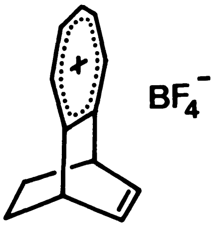
A series of tropylium ions incorporated into bicyclo[2.2.1]heptane skeleton having exo-methylene π-system, 1,2,3,4-tetrahydro-1,4-ethylidenebenzotropylium salts, has been synthesized and their charge-transfer interaction and the thermodynamic stability have been examined.

In our recent studies on the synthesis and intramolecular charge-transfer (CT) phenomena of some bicyclic compounds which consist of the donor and acceptor components with rigid and nonparallel spatial arrangement, we have described the synthesis of 1,4-dihydro-1,4-ethano- (1)[1] and 1,4-dihydro-1,4-ethenobenzotropylium tetrafluoroborate salts (2)[2] and their CT phenomena between the tropylium ion and remote ethylenic π-system. In this paper we wish to report our study on the title compounds 3 in which the donor ethylene π-system is in more disadvantageous position than in 1 and 2 with respect to spatial orbital overlap between two π-systems.



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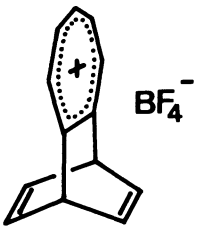

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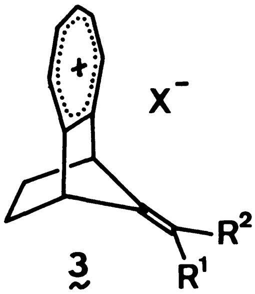
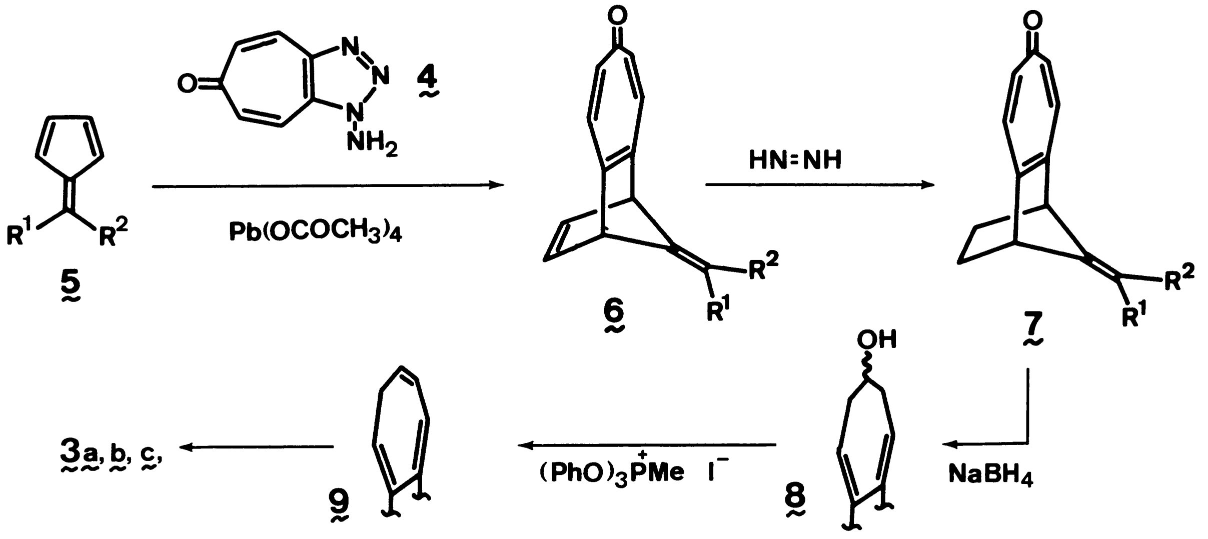


3

a, $R^1 = R^2 = Me$; BF_4^-
b, $R^1 = H$; $R^2 = Ph$; ClO_4^-
c, $R^1 = R^2 = Ph$; BF_4^-

We have previously developed a facile synthetic method for construction of the bridged tropylium ion which is based on the Diels-Alder reaction of 4,5-dehydrotropone[3] generated in situ with appropriate diene and subsequent conversion of the tropone ring into the tropylium ion.[4] Application of this method to fulvenes is expected to give the desired skeleton leading to 3. Thus, reaction of 1-amino-6(1H)-cycloheptatriazolone (4)3) with an equivalent of lead tetraacetate in the presence of a large excess of 6,6-dimethylfulvene (5a) in dichloromethane at 0 °C for 3 h gave the adduct 6a5) in 40% yield which was reduced with diimide (KOOCNNCOOK/MeOH/AcOH, rt.) to give 7a5) in 46% yield. Reduction of 7a (NaBH$_4$/H$_2$O-MeOH, rt., overnight) gave an epimeric mixture of the alcohol 8a5) in 65% yield. Dehydration of 8a to the tropilidene 9a5) was best achieved with methyltriphenoxyphosphonium iodide6) in HMPA, which gave 9a at 50 °C for 1.5 h under nitrogen in 46% yield. Final conversion of 9a into the tropylium ion 3a7) was carried out by usual hydride abstraction with trityl tetrafluoroborate. The cation salts 3b8) and 3c9) were also obtained in a similar manner. Because of the highly hygroscopic nature of its tetrafluoroborate salt, the cation 3b was isolated as the perchlorate in a pure form.



In the electronic spectra in dichloromethane shown in Figure 1, the cation 3a, 3b, and 3c exhibit long wavelength absorption bands at 374, 388, and 416 nm, respectively,10) which show marked blue shift to 358, 368, and 387 nm upon changing the solvent to more polar acetonitrile.

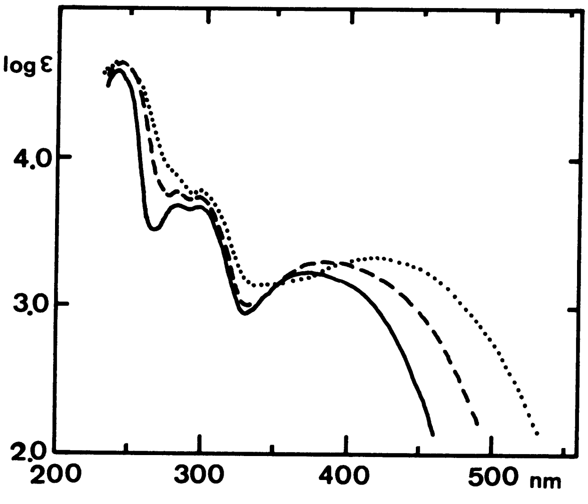


Figure 1. Electronic spectra of 3a (——), 3b (– – –), and 3c (·······) in dichloromethane.

These observations together with the concentration independence of the absorption intensities suggested that the bands observed in the long wavelength region are to be assigned to the intramolecular CT transitions between exocyclic methylenes and the remote tropylium moieties.

This assignment is further supported by the substituent effect; for a series of tropylium ions **3** there is a progressive red shift of the absorption maximum in the long wavelength region with decreasing ionization potentials of the donor moieties, 1,1-dimethylethylene (9.45 eV),11) styrene (8.50 eV),12) and 1,1-diphenylethylene (8.25 eV).12,13)

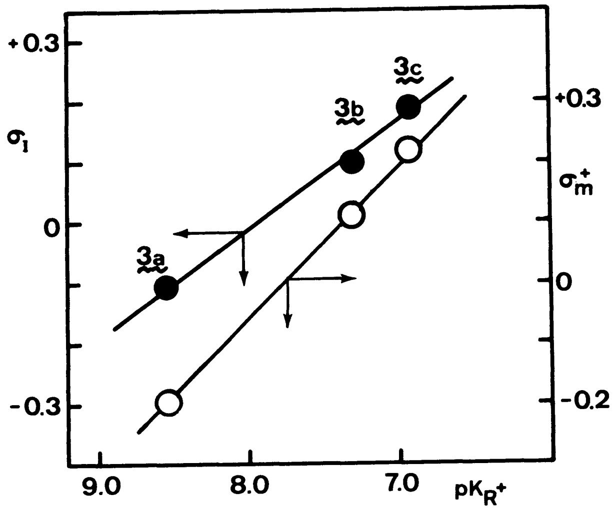


Figure 2. Plots of pK_{R^+} values for **3a**, **3b**, and **3c** against σ_I and σ_m^+ values of the substituents on the exocyclic double bond.

In order to examine the thermodynamic stability of **3**, the pK_{R^+} values were determined spectrophotometrically in 20% aqueous acetonitrile. It is apparent that the stability of the tropylium ion is substantially enhanced in **3a** (pK_{R^+} = 8.55) compared with **3b** (pK_{R^+} = 7.32) and **3c** (pK_{R^+} = 6.92). This trend can be attributed to the increase in the electron donating inductive effect of the substituents on the bridged exocyclic methylene moiety. This is further supported by the fact that the plots of the pK_{R^+} data against the sum of σ_m^+ 14) or σ_I 14) for the substituents on the exocyclic methylene group provide good straight lines (correlation coefficient, 0.9998 and 0.9954, respectively) as shown in Figure 2. Like the tropylium ions such as **1**1) and **2**,2) a dominant factor affecting the thermodynamic stability of the present system is also the electron donating inductive effect of the bridged segment and the stabilization by electron supply from the remote ethylene π-system would not be significant in the ground-states of these molecules.

References

1) T. Nakazawa, Y. Niimoto, K. Kubo, and I. Murata, Angew. Chem. Int. Ed. Engl., 19, 545 (1980).

2) T. Nakazawa, K. Kubo, and I. Murata, Angew. Chem. Int. Ed. Engl., 20, 189 (1981).

3) T. Nakazawa and I. Murata, Angew. Chem. Int. Ed. Engl., 14, 711 (1975).

4) T. Nakazawa and I. Murata, J. Am. Chem. Soc., 99, 1996 (1977).

5) All new compounds reported gave satisfactory elemental analyses and/or exact mass measurements and spectroscopic data.

6) J. P. H. Verheyden and J. G. Moffatt, J. Org. Chem., 35, 2319 (1970).

7) **3a**, pale yellow needles, mp 110-111 °C (d.); ^{1}H-NMR (CD_2Cl_2) 1.46 (q-like, 2H), 1.69 (s, 6H), 2.27-2.55 (m, 2H), 4.52 (t-like, 2H), 8.81-9.05 (m, 5H), ^{13}C-NMR (CD_3CN) 20.1, 25.0, 51.3, 122.1, 146.0, 146.0, 149.2, 153.6, 177.8.

8) **3b**, yellow needles, mp 150-152 °C; ^{1}H-NMR (CD_2Cl_2) 1.60 (q-like, 2H), 2.65 (d-like, 2H), 4.43 (s-like, 1H), 4.90 (s-like, 1H), 6.41 (s, 1H), 7.31 (m, 5H), 9.00 (m, 5H); ^{13}C-NMR (CD_3CN) 24.7, 25.1, 50.7, 55.4, 128.6, 129.2, 129.7, 136.5, 140.3, 146.6, 146.8, 149.8, 153.3, 154.0, 154.1, 176.7, 176.8.

9) **3c**, yellow scales, mp 188.5-190.5 °C (d.); ^{1}H-NMR (CD_2Cl_2) 1.59 (d-like, 2H), 2.62 (d-like, 2H), 4.54 (t-like, 2H), 7.01-7.43 (m, 10H), 8.99 (br.s, 5H); ^{13}C-NMR (CD_3CN) 24.9, 52.8, 128.7, 129.3, 130.1, 132.8, 140.5, 146.5, 149.7, 150.3, 154.1, 176.8.

10) 1,2,3,4-Tetrahydro-1,4-methanobenzotropylium ion, which is regarded as a reference compound for **3a**, **b**, and **c**, showed maxima at 237 nm (log ε 4.47), 280 (3.53), and 298 (3.59), and no CT-band was observed. K. Okamoto, K. Takeuchi, K. Komatsu, Y. Waki, R. Ohara, and S. Shirai, J. Chem. Soc., Perkin 2, submitted for publication. We are grateful to Professor Kunio Okamoto, Kyoto University, for communicating the data prior to publication.
K. Komatsu, Y. Waki, R. Ohara, S. Shirai, Y. Kubota, and K. Takahashi, J. Chem. Soc., Perkin 2, submitted for publication. We are grateful to Professor Kunio Okamoto, Kyoto University, for communicating the data prior to publication.

11) K. Kimura, S. Katsumata, T. Yamazaki, and H. Wakabayashi, J. Electron Spectrosc., 6, 41 (1975).

12) J. P. Maier and D. W. Turner, J. Chem. Soc., Faraday Trans 2, 69, 196 (1973).

13) In the long wavelength region of weak absorption (320-450 nm), both **3a** and **3c** show magnetic circular dichroism spectral (MCD) extrema; 395 nm and 335 nm for the former, 435 nm and 345 nm for the latter. This implies, at least, two electronic origins associated with the longest wavelength absorption of 3.
For the detailed MCD spectra and the theoretical consideration, see A. Tajiri, M. Hatano, T. Nakazawa, K. Nakasuji, and I. Murata, Ber. Bunsenges, Phys. Chem., in press.

14) The values for σ_m^+ and σ_I were taken from J. March, "Advanced Organic Chemistry", 2nd Ed., McGraw-Hill, New York, N. Y., 1977, p. 253 and p. 256.

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