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A NOVEL HETEROCYCLE COMPOSED OF CALICENE AND CYCLOPROPENONE HYDRAZONE UNITS -------3,8-BIS(*t*-BUTYLTHIO)-5,6-DIAZATETRACYCLO-[8,3,0,$0^{2,4}$,$0^{7,9}$]TRIDECA-1,3,6,8,10,12-HEXAENE

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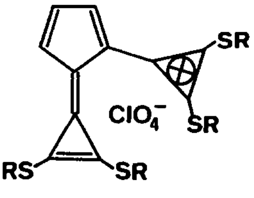
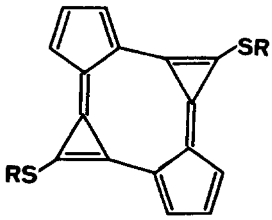
Abstract: The titled compound (3) is synthesized by the reaction of 1,2-bis(dithiocyclopropenylio)cyclopentadienide with hydrazine. The ^{1}H- and ^{13}C-NMR spectra suggest significant contribution of a novel polarized structure (3B) compared with a peripheral 14π conjugation structure (3A). Reaction features of 3 are also examined.

Very recently we reported synthesis of a novel doubly cross-conjugated cation, 1,2-bis(dithiocyclopropenylio)cyclopentadienide (1) from 5,6-bis-(*t*-butylthio)calicene and 1,2-bis(*t*-butylthio)-3,3-dichlorocyclopropene.[1] Since 1 possesses alkylthio groups of good leaving nature, it might be possible to synthesize new polycyclic π-conjugated systems by the reaction of 1 with appropriate nucleophiles. As an example of such sort, we succeeded in synthesis of a novel polycyclic aromatic system having peripheral 16π electrons, 3,11-bis(*t*-butylthio)cyclic bicalicene (2)[2,3] from 1 and cyclopentadienide. This communication describes another example, that is,



1



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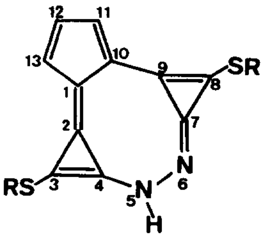
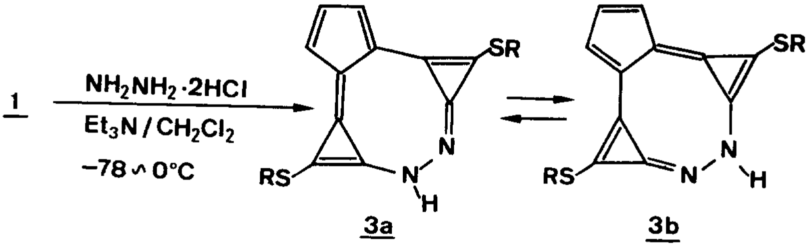


3

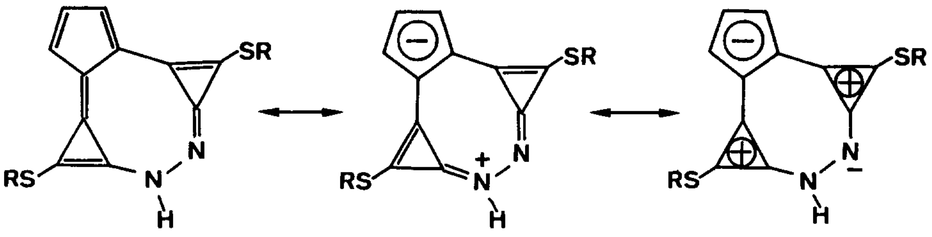
R=*t*-Bu

synthesis of a novel polycyclic cross-conjugated heterocycle, the titled compound (3) which is composed of a calicene (8π) unit and a cyclopropenone hydrazone (6π) unit, and possesses a possible peripheral 14π conjugation structure.

The titled compound can be synthesized as shown below. Thus, reaction

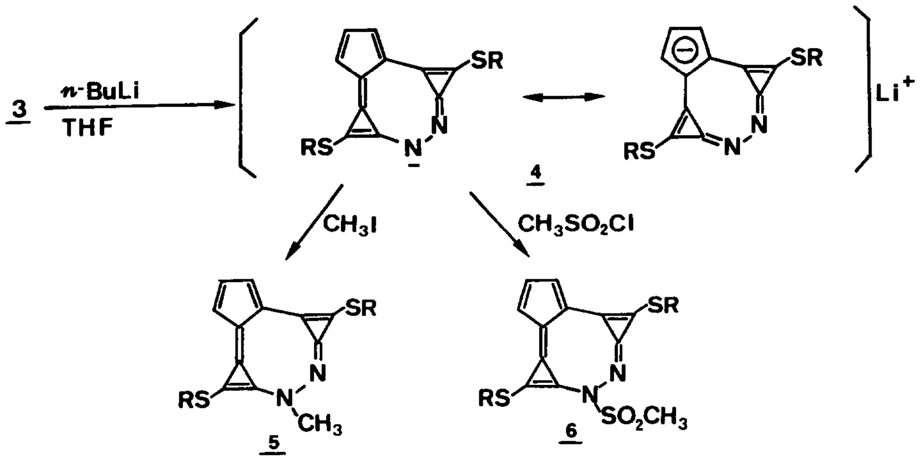


of 1 with an equimolar amount of hydrazine dihydrochloride in dichloromethane in the presence of triethylamine at -78°C afforded 3 as pale yellow solid: mp 80-82°C (43% yield); IR (KBr) 1840, 1522 cm^{-1}; UV (CH_2Cl_2) λ_{max} (logε) 242 (4.31), 280 (4.04), 340 (sh, 4.08), 374 nm (4.28); ^1H-NMR ($CDCl_3$, ppm)δ 7.20 (d, 2H, $H_{11,13}$, J=3.6 Hz), 6.94 (t, 1H, H_{12}, J=3.6 Hz), 1.70 (s, 18H, *t*Bu)[4]; ^{13}C-NMR ($CDCl_3$, ppm)δ 129.1 ($C_{11,13}$), 122.2 (C_{12}), 121.3 ($C_{3,8}$), 115.8 ($C_{2,9}$), 114.2 ($C_{4,7}$), 107.7 ($C_{1,10}$), 47.9 ($\underline{C}(CH_3)_3$), 31.5 ($C(\underline{C}H_3)_3$); MS calcd for $C_{19}H_{22}N_2S_2$: m/e (M^+) 342.1225, found: 342.1240. The facts that the H_{11} and H_{13} protons are observed as magnetically equivalent one in the ^1H-NMR spectrum, and that the ^{13}C-NMR spectrum consists of eight carbon signals, clearly indicate that 3 is in a fast equilibrium between two tautomers, 3a and 3b. Interestingly, the ^1H-signals of cyclopentadienide part of 3 appear at almost the same region to those of the thione derivative of 1 which is an acyclic system with an isoelectronic π-structure to 3 (δ 7.22 ∿ 6.50 ppm)[3,5], indicating that the former compound does not possess a diamagnetic ring current due to peripheral 14π structure. The ^{13}C-signals of cyclopentadienyl part of 3 appear at the similar region to those of 2,[6] suggesting the contribution of a polar structure.[2] While, the ^{13}C-signals of cyclopropenyl ring are observed at the considerably higher magnetic field compared with those of 2, suggesting that 3B rather than 3C mainly contributes in the polar structure of 3. Consequently, the ground state of 3 is more suitably expressed by a novel polarized structure (3B)[7] than by a peripheral 14π conjugation structure (3A). This contrasts dramatically with the stabilization in pyrazole where peripheral 6π conjugation structure involving a hydrazone moiety contributes dominantly to the ground state.



3A 3B 3C

Treatment of 3 with *n*-butyllithium at room temperature gave the corresponding lithium amide (4). The ^{1}H-NMR spectrum in d_8-THF shows signals at δ 6.80 (d, 2H), 6.50 (t, 1H) and 1.62 (s, 18H), from which a diamagnetic ring current due to peripheral 14π conjugation is not expected, because the cyclopentadienyl protons appear at upper magnetic field by ca. 0.4 ppm compared with those of 3. When 4 was allowed to react with iodomethane and methanesulfonyl chloride, N-methyl (5) and N-methanesulfonyl (6) substituted derivatives were obtained in respective yields of 40 and



35%,[8] along with uncharacterized tarry materials derived by attack of nucleophiles toward the cyclopentadienyl ring.

References and Notes

1. Z. Yoshida, M. Shibata, S. Kida, S. Miki, T. Sugimoto and S. Yoneda, *Tetrahedron Lett.*, 25, 345 (1984).
2. S. Yoneda, M. Shibata, S. Kida, Z. Yoshida, Y. Kai, K. Miki and N. Kasai, *Angew. Chem.*, 96, 75 (1984); Z. Yoshida, *Pure Appl. Chem.*, 54, 1059 (1982).
3. Z. Yoshida, M. Shibata, F. Iwasaki, S. Yoneda and T. Sugimoto, submitted to *J. Am. Chem. Soc.*
4. It should be ascribed to fast tautomerism between 3a and 3b that N-H signal does not sharply appear.
5. The thione derivative of 1 was synthesized by the reaction of 1 with sodium bicarbonate in refluxing ethyl acetate in 54% yield.[3]
6. The NMR spectral data of 2 are as follows: ^{1}H-NMR ($CDCl_3$, ppm)δ 6.87 (d, 4H, $H_{6,8,14,16}$, J=3.8 Hz), 6.40 (t, 2H, $H_{7,15}$, J=3.8 Hz), 1.75 (s, 18H, *t*Bu); ^{13}C-NMR ($CDCl_3$, ppm)δ 135.9 ($C_{2,4,10,12}$), 128.2 ($C_{3,11}$), 127.5 ($C_{6,8,14,16}$), 123.0 ($C_{7,15}$), 109.0 ($C_{1,5,9,13}$), 48.0 ($\underline{C}(CH_3)_3$), 31.6 ($C(\underline{C}H_3)_3$).
7. The protonation of 3 with trifluoroacetic acid selectively occurred at the cyclopentadienyl ring to give the conjugate acid. The ^{1}H-NMR spectrum shows the signals at δ 7.49 (bs, 2H), 4.15 (bs, 2H) and 1.80 (s, 18H, *t*Bu).
8. 5: pale yellow crystals, mp 121-122°C(dec.); IR (KBr, cm^{-1}) 1840, 1532; ^{1}H-NMR ($CDCl_3$, ppm)δ 7.15 (m, 2H), 6.93 (t, 1H), 3.90 (s, 3H, Me), 1.82 (s, 9H, *t*Bu), 1.71 (s, 9H, *t*Bu). 6: pale yellow crystals, mp 117-119°C (dec.); IR (KBr, cm^{-1}) 1835, 1532; ^{1}H-NMR ($CDCl_3$, ppm)δ 7.35 (dd, 1H), 7.22 (dd, 1H), 6.95 (t, 1H), 3.50 (s, 3H, Me), 1.82 (s, 9H, *t*Bu), 1.73 (s, 9H, *t*Bu).

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