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Y-AROMATIC DICATIONS AND STABILIZED TRIMETHYLENEMETHANES

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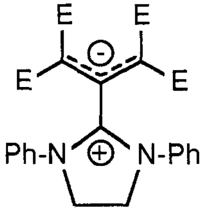
Summary: Calculated heats of formation of thio and amino substituted planar triplet trimethylenemethanes are comparable to those of the corresponding methylenecyclopropanes. Y-Aromatic [1]-tris(1,3-dithiol-2-yl)[0.0.0]monomethinium bistetrafluoroborates, prepared via novel 6.6-diformyl-1,3-dithiafulvenes and the corresponding bisdithioacetals, can be reversibly reduced to stable radical cations and neutral compounds tentatively assigned as stable trimethylenemethanes.

The interesting theoretical models for ferromagnetic organic materials put forward by McConnell[1], Breslow[2], Wudl[3], Miller and Epstein[4] and Torrance[5] are a challenge for the organic chemist (ferromagnetism in polyradicals cf.[6-8]). In essence, McConnell's idea is to prepare ionic charge-transfer salts ...D^+A^-... in which the D^+A^- pair through back-charge-transfer excitation to a neutral triplet state could also be a triplet leading to ferromagnetic coupling of the spins of adjacent ions. Antiaromatic ions (hexaaminobenzene dication salts[2], cyclopentadienyl cations[9], stable, crystalline cyclopentadienylium salts[10,11]) are candidates for this model. Triplet trimethylenemethanes[12-14] are interesting in this respect as well. A stabilization of these notoriously unstable 4π-electron "anti-Y-aromatic" systems (Y-aromaticity, cf.[15,16]) can be achieved by way of donor-acceptor substitution: **1**-**4** are crystalline compounds having, however, singlet ground states as expected.[17,18] Thus, the problem is to design trimethylenemethanes in which the triplet character of the parent compound is preserved and the ring closure to methylenecyclopropanes prevented.



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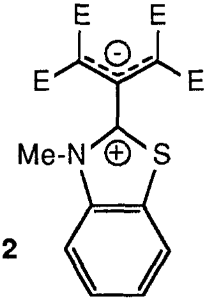

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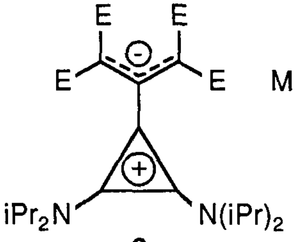

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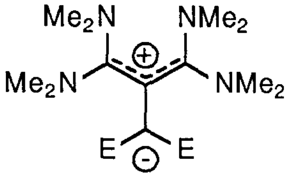
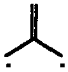
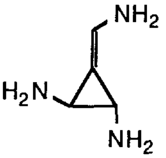
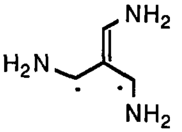
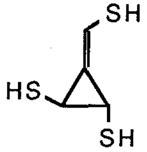
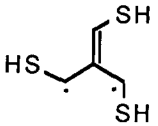
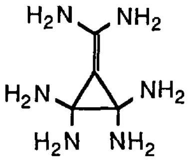
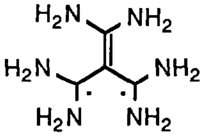
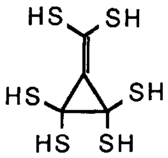
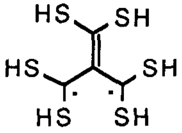


4

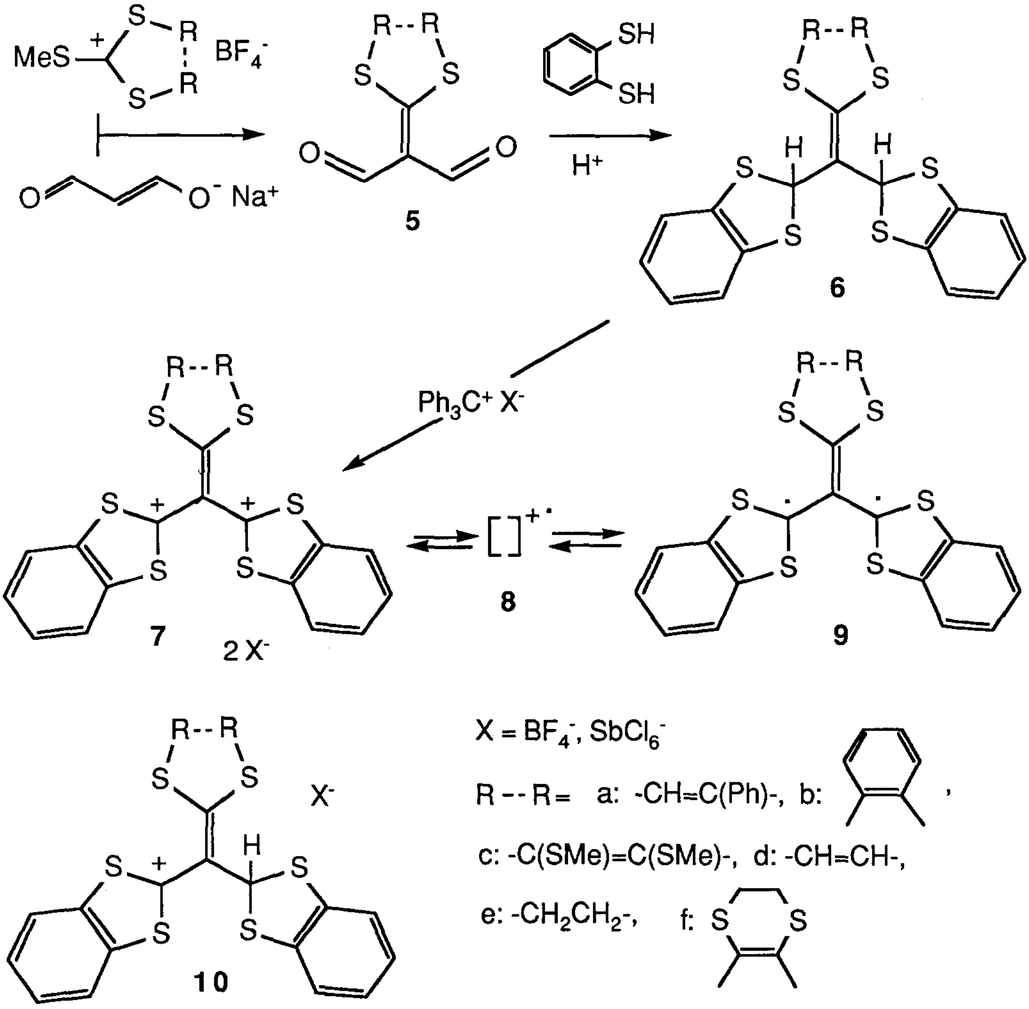
E = CO_2Me

INDO-CI calculations demonstrate that planar trimethylenemethane is more stable as a triplet than as a singlet.[16] MNDO/CI calculations lead to the same result (cf. Table 1). Thio and amino substituted planar triplet trimethylenemethanes are also more stable than the corresponding singlets. In contrast to the parent system where methylenecyclopropane is much more stable than triplet trimethylenemethane the energies of the thio and amino substituted triplet trimethylenemethanes are in the same order of magnitude as those of the corresponding singlet methylenecyclopropanes (due to steric hindrance, the hexasubstituted trimethylenemethanes are less stable than the corresponding methylenecyclopropanes). Thus, systems of this sort are promising candidates for the preparation of stable triplet trimethylenemethanes. As thio groups stabilize positive and negative charges (carbenium ions and carbanions) thio substituted Y-shaped dications and dianions (cf. Y-aromatic dianions[19] and dications[20-25]) are natural precursors for the type of trimethylenemethanes listed in Table 1 (formation of trimethylenemethanes from methylenecyclopropanes, cf.[26]).

Table 1 Heats of formation of trimethylenemethanes and methylenecyclopropanes (H_f [kcal/mol]; MNDO/CI)

singlet		singlet	triplet
39.6	 	88.6	53.3
72.0	 	92.3	63.3
55.5	 	89.0	57.0
104.7	 	175.0	151.3
83.0	 	127.5	98.1

Starting materials for the preparation of thio substituted trimethylenemethanes are the methylenemalonaldehydes[27] **5**, the first 6,6-diformyl-1,3-dithiafulvenes. Alkylidenemalonaldehydes, for the first time prepared by Woodward[28] during the synthesis of cephalosporine C, have gained new interest following the syntheses of benzylidene- and polyenylidenemalonaldehydes[29,30] and cycloheptatrienylidenemalonaldehyde.[31] **5a-d,f** can readily be obtained from the sodium salt of malonaldehyde and 2-methylthio-1,3-dithiolium salts (2-methylthio-1,3-dithiolanylium tetrafluoroborate in case of **5e**) in acetonitrile at room temperature. Treatment of **5a-c** with o-benzenedithiol in methanol in the presence of 54% $HBF_4{\cdot}Et_2O$ furnishes the dithioacetals[27] **6** in moderate yields (cf.[32]; Wudl[22] has synthesized some saturated derivatives of **6** starting from triformylmethane). Compounds **6** can be oxidized with trityl salts to form the Y-aromatic dication salts[27] **7a,b**, X = BF_4, and **7c**, X = $SbCl_6$. Oxidation of **6b,c** gives mixtures of **7b** and **10b**, X = BF_4, and **7c** and **10c**, X = $SbCl_6$, respectively, which in case of **7c/10c** can be separated (different solubilities in acetonitrile).



X = BF_4^-, $SbCl_6^-$

R--R= a: -CH=C(Ph)-, b: ,

c: -C(SMe)=C(SMe)-, d: -CH=CH-,

e: $-CH_2CH_2-$, f:

The cyclovoltammograms (10^{-3} M in dry acetonitrile with 0.1 M nBu_4NPF_6, vs. Ag/AgCl) of **7** show two pairs of reversible waves (**7a**: -0.02, -0.32 V; **7b**: 0.03, -0.23 V; **7c**: insufficient solubility) stemming from one-electron processes. As even the second step **8** → **9** of the reduction is perfectly reversible we assign the trimethylenemethane structure **9** to the product instead of that of a methylenecyclopropane. ESR studies as to the properties of **9** are under way.

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27) **5a**: Yield 59%; m.p. 193-194 °C; ^1H NMR ($CDCl_3$, 80 MHz): $\delta = 7.35-7.65$ (m; 6 H, H-5, phenyl-H), 9.75 (s; 2 H, CHO); IR (KBr): 1608 cm^{-1}, 1389, 1221, 751, 720, 560; UV (CH_2Cl_2): λ_{max} (log ε) = 236 nm (4.43), 266 (4.03), 295 (3.69), 404 (4.47). **5b**: 45%; m.p. 231-232 °C. **5c**: 45%; m.p. 166-167 °C. **5d**: 61%; m.p. 255-256 °C; ^1H NMR ($CDCl_3$): $\delta = 7.60$ (s, 2 H, H-4,5), 9.80 (s; 2 H, CHO). **5e**: 45%; m.p. 132-133 °C. **5f**: 62%; m.p. 237-238 °C. **6a**: 40%; m.p. 194-195 °C; ^1H NMR ($CDCl_3$, 80 MHz): $\delta = 6.53$ (s; 1 H, H-5), 6.59 (s; 2 H, SCHS), 6.95 (mc; 13 H, phenyl-H, benzo-H)); IR (KBr): 2870 cm^{-1}, 1444, 1116, 739, 689, 674. **6b**: 41%; m.p. 243-244 °C. **6c**: 35%; m.p. 212-214 °C. **7a**, X = BF_4: 45%; m.p. 238-240 °C; ^1H NMR (CD_3CN, 80 MHz): $\delta = 7.89$ (mc; 5 H, phenyl-H), 8.30 (mc; 4 H, benzo-H), 8.75 (mc; 4 H, benzo-H), 9.43 (s ; 1 H, H-5); IR (KBr): 1378 cm^{-1}, 1084, 761, 734, 680; UV (CH_3CN): λ_{max} (log ε) = 228 nm (4.69), 372 (3.90), 492 (4.82). **7b** + **10b**, X = BF_4: .m.p. 240-243 °C. **7c**, X = $SbCl_6$: m.p. 181-182 °C. **10c**, X = $SbCl_6$: m.p. 170-172 °C.
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