Unusual conversions of a zwitterionic polyfused triazine with electron-deficient dienophiles

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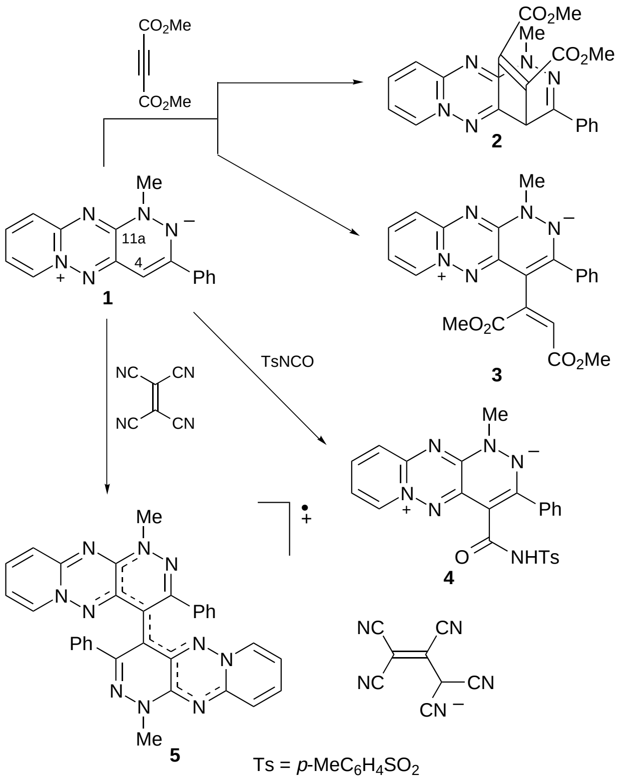
Investigation of reactions of the zwitterionic polycycle 1 with electron-deficient dienophiles revealed that Michael addition products 3 and 4, selective cycloadducts 2 and, in a special case, a stable dimeric radical cation 5 are formed.

As a result of our investigations on ring transformation reactions[1] with furo[2,3-*e*]pyrido[1,2-*b*][1,2,4]triazinium salts[2] we synthesized some new zwitterionic polyazaheterocycles (*e.g.* the 1,3-disubstituted pyrido[1,2-*b*]pyridazino[3,4-*e*]-[1,2,4]triazine derivative **1**), the reactivity of which towards dienophiles, because of their highly dipolar character seemed of particular interest. We decided to investigate the reactivity of the new derivative **1** with three different dienophiles (*i.e.* dimethyl acetylenedicarboxylate, toluene-*p*-sulfonyl isocyanate and tetracyanoethylene) (Scheme 1).

We found that zwitterion **1**, when treated with dimethyl acetylenedicarboxylate at room temperature in CH_2Cl_2 for 24 h, afforded a mixture of two components (1 : 1), which were separated by chromatography (silica, chloroform–methanol, 25 : 1). Structure elucidation of the more polar component (a pale yellow spot by TLC) by ^1H NMR spectroscopy revealed the formation of the bridged [3 + 2]-cycloadduct **2**,†‡ whereas the less polar product (a brown–red spot) was proved *via* an X-ray analysis (Fig. 1) to be the Michael adduct **3**.†§ The X-ray data confirmed the *Z* configuration at the exocyclic double bond, as well as a strong predominance of the mesomeric form outlined on Scheme 1. The selective formation of cycloadduct **2** seemed to be in agreement with the results of the FMO analysis of this compound: positions 4 and 11a had the highest c_{LUMO} values (0.6 and 0.54, respectively). Formation of Michael addition products was again experienced when **1** was reacted with toluene-*p*-sulfonyl isocyanate, thus exclusively affording compound **4**.¶

An unexpected result was obtained from the reaction of tricycle **1** with tetracyanoethylene. A blue crystalline compound was obtained, which could not be analysed by NMR spectroscopy. An X-ray investigation (Fig. 2) revealed the structure of compound **5** containing a highly delocalized radical cation, as established by EPR spectroscopy.‖ The central 'formal' C=C bond is the longest [C(1)–C(21) = 145.9 pm] of all the C–C bonds present in **5**.** The two tricyclic fused triazine units are highly twisted [torsion angle C(2)–C(1)–



Scheme 1

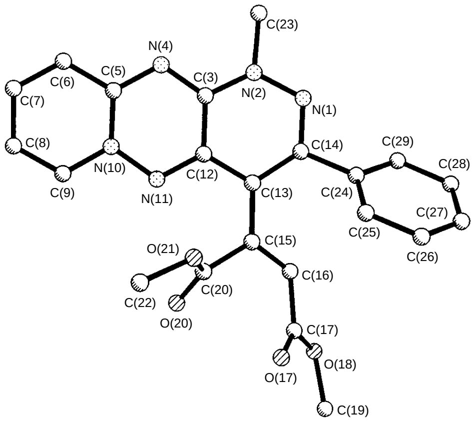


Fig. 1 Stereoview of **3**

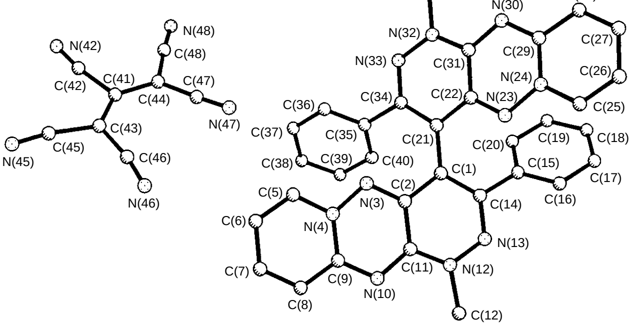


Fig. 2 Stereoview of **5**

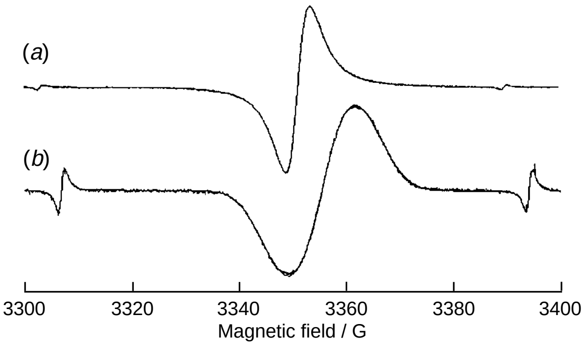


Fig. 3 Calculated and experimentally found EPR spectra of **5** in (*a*) the solid and (*b*) the solution states

C(21)–C(22) = 131.3°] and arranged in an *anti* conformation. Formation of this unusual product can be rationalized by the primary attack of the reagent at position 4, followed by an oxidative coupling to the dimer radical cation which is stabilized by the pentacyanopropenide anion.[3,4] These anions are usually obtained either from dimerization of tetracyanoethylene under basic conditions[5] or through base-catalysed addition of malononitrile to tetracyanoethylene.[6]

The EPR spectrum of **5** (Fig. 3) showed one broad singlet, and dilution and degassing did not produce any hyperfine structure. Computer fitting of the line profile (Fig. 3) gave a perfect fit if proton splittings are removed from the AM1 calculations,[7] while the K proportionality constant for nitrogen is adjusted (K_N = 2340) in the hyperfine coupling *versus* spin density relation $A_N = K_\rho$). The largest nitrogen coupling (2.6 G) is reasonable for the dimer cation radical when compared to the largest nitrogen coupling (7.1 G) in the monomeric cation radical of isoalloxanine,[8] and the observed g factor (2.0037) is also typical for cation radicals.[9] No EPR signal for an anion radical (g = 2.0026, well resolved hyperfine structure[10]) was detected.

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Footnotes

† All new compounds gave spectroscopic and analytical data in accordance with their assigned structures.

‡ *Selected spectroscopic data* for **2**: Pale Yellow Crystals, mp 218–20 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (1 H, d, H-7), 7.75, 7.35–7.30 (5 H, m, Ph), 7.25 (1 H, t, H-9), 7.06 (1 H, d, H-10), 6.52 (1 H, t, H-8), 4.84 (1 H, s, H-4), 3.83, 3.80 (6 H, s, CO_2Me), 3.27 (3 H, s, Me).

§ *Selected spectroscopic data* for **3**: Brown–red crystals, mp 198–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$— δ 7.32 (1 H, d, H-7), 7.30 (5 H, m, Ph), 7.05 (1 H, t, H-9), 7.02 (1 H, t, H-8), 6.30 (1 H, d, H-10), 5.83 (1 H, s, H-2′), 3.58, 3.42 (6 H, s, COMe), 3.13 (3 H, s, Me).

X-Ray crystallographic analysis of **3**. The brown–red crystal was grown by slow evaporation of an acetonitrile solution of **3**. The crystal was monoclinic, space group *C*2/*c*, with cell dimensions a = 1917.5(7), b = 838.6(3), c = 2561.1(9) pm and V = 4051(2) × 10^6 pm^3. Z = 8 molecules ($C_{22}H_{18}N_5O_4$, M_w = 417.43) in the unit cell (D_c = 1.369 g cm^{-3}). Intensity data were measured for 6448 reflections (4651 unique) on a Siemens R3m/V diffractometer using a crystal with dimensions 0.4 × 1.3 × 0.25 mm (Mo-Kα radiation, graphite monochromator, Wyckoff-scan, θ range = 1.75–27.5°, linear absorbtion coefficient = 0.09 mm^{-1}, absorbtion correction: Ψ-scan). The structure was solved by direct phase determination and refined by full-matrix-least square analysis using Siemens SHELXTL PLUS (Micro VAX II); all hydrogen positions of riding model had fixed isotropic U. The data-to-parameter ratio was 12.83, R, R_w = 0.054, 0.049; weighting scheme $w = 1/\sigma^2(F)$. The largest difference peak and hole in the last map were 0.32 and 0.21 e Å 4^{-3}, respectively.

¶ *Selected spectroscopic data* for **4**: Brown–red crystals, mp 228–230 °C (DMF); IR (KBr) ν/cm^{-1} 3180, 3040, 2920, 1660, 1620, 1590, 1560, 1530.

‖ *Selected spectroscopic data* for **5**: Blue crystals, mp 240–42 °C; IR ν(KBr)/cm^{-1} 2196, 1627, 1561, 1508.

** *X-Ray crystallographic analysis* of **5**: The dark blue crystal was triclinic, space group $P\bar{1}$, with cell dimensions a = 1299.7(2), b = 1349.7(2), c = 1078.0(2) pm, α = 92.31(1), β = 95.88(1), γ = 99.70(1)° and V = 1850.9(5) × 10^6 pm^3. Z = 2 molecules ($C_{32}H_{24}N_{10}$ + C_8N_5, M_w = 376.38) in the unit cell (D_c = 1.282 g/cm^{-3}). Intensity data were measured for 8485 reflections (8485 unique) on a Siemens R3m/V diffractometer using a crystal with dimensions 0.5 × 0.7 × 0.15 mm (Mo-Kα radiation, graphite moinochromator, Wyckoff-scan, θ range 1.75–27.5°, linear absorbtion coefficient = 0.08 mm^{-1}, absorbtion correction: Ψ-scan). The structure was solved by direct phase determination and refined by full-matrix least-squares analysis using Siemens SHELXTL PLUS (MicroVAX II); all hydrogen positions of riding model had fixed isotropic U. The data-to-parameter ratio was 12.14, R, R_w = 0.076, 0.069, respectively; weighting scheme $w = 1/\sigma^2(F)$. The largest difference peak and hole in the last map were 1.01 and 0.46 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/410.

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