

SYNTHESIS AND STRUCTURE OF
4,5,6-TRIMETHYL-1-OXO-1H-1,2,4-TRIAZOLO[1,2-a]PYRAZOL-4-IUM-3-OLATE,¹
A NEW MESOIONIC 4n π -HETEROCYCLE

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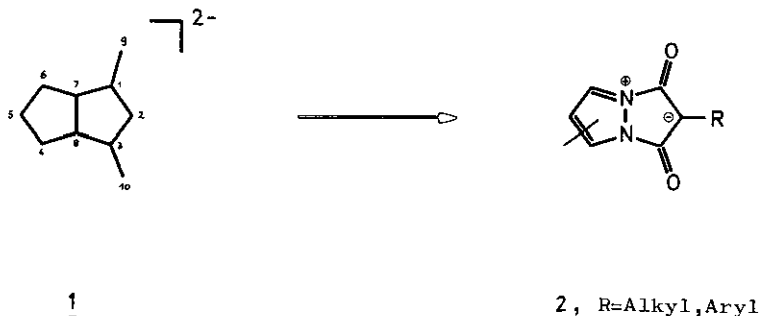
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Dedicated to Prof Dr phil Alexander Schönberg
on the occasion of his 90th birthday

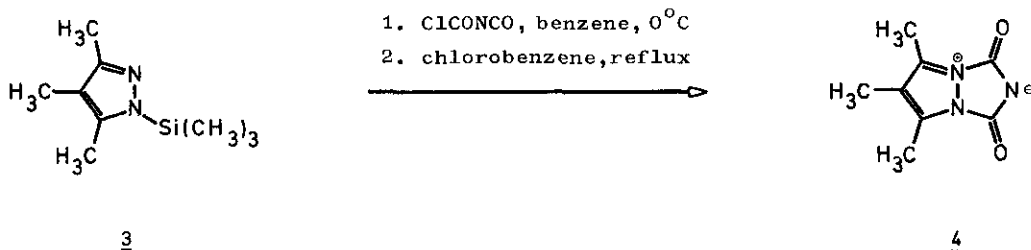
ABSTRACT — Synthesis, structure, and reactions of the
title compound are described.

1,3-Pentalenylenbismethyl dianion (1) is the isoconjugated basis system of a new
class of mesoionic compounds which recently came to light²⁻⁴.



The introduction of nitrogen atoms at positions 7 and 8 as well as oxygen atoms at positions 9 and 10 leads to a system (2) which is either available from pyrazoles and malonyl dichlorides (chlorocarbonylketenes)^{2,3} or by the reaction of 3,5-dihydroxypyrazoles with 1,3-dicarbonyl compounds like 2,4-pentanedione or suitable derivatives thereof⁵.

In this communication the preparation and structure of an aza-analogue of 2 (4) is described.



Whereas the direct reaction of 3,4,5-trimethylpyrazole with chlorocarbonyl isocyanate⁷ was unsuccessful, treatment of the activated⁸ pyrazole 3⁹ with this 1,3-bielectrophile in benzene at 0°C yields a precipitate, which on heating in chlorobenzene is transformed to 4 (35% colorless rhombs with mp 161.5-162°C; IR(KBr): 1715 (s), 1725 (s), 1801 (m), 2927 cm⁻¹; UV(CH₃CN): λ (log ε) = 233 (4.139), 238.5 (4.136), 247 (sh, 4.049), 255.5 (sh, 3.792), 288.5 nm (plateau, 2.615); ¹H-NMR (CDCl₃): δ = 2.06 (s, 5-CH₃), 2.57 ppm (s, 4-CH₃, 6-CH₃); ¹³C-NMR(CDCl₃): δ = 7.47 (q), 9.81 (q), 121.86 (C-5), 141.55 (C-4, C-6), 150.19 ppm (C-1, C-3)). It is of interest to note that the ¹³C-signal of C-4 (C-6) appears in the same region as the corresponding absorption in 3,4,5-trimethylpyrazole¹⁰. Compound 4 is moderately stable in air, but is instantaneously hydrolyzed in moist THF to give a quantitative yield of 5. Treatment of 4 with trimethyloxonium tetrafluoroborate yields 6¹¹



(84% colorless prisms with mp 133°C; IR(KBr): 1791 (s), 1848 cm⁻¹ (m); UV(CH₃CN): λ (log ε) = 233.5 (4.234), 235 (4.233), 239 (sh, 4.219), 250 (sh, 3.972), 307 nm

(3.459); $^1\text{H-NMR}$ (CD_3CN) : δ = 2.12 (s, 5- CH_3), 2.70 (s, 4- CH_3 , 6- CH_3), 3.25 ppm (s, N- CH_3); $^{13}\text{C-NMR}$ (CD_3CN) : δ = 7.44 (q), 11.05 (q), 27.68 (q), 126.37 (C-5), 142.91 (C-4, C-6), 151.85 ppm (C-1, C-3)).

The UV spectrum of 4 is considerably shifted to the short wavelength region compared to 2²⁻⁴. This phenomenon can easily be rationalized by using PMO arguments. As can be seen from Fig.1 the introduction of an electronegative nitrogen atom in position



FIG. 1 HOMO and LUMO of 1,3-Pentalenylenbismethyl Dianion (HMO values).

2 lowers HOMO but leaves LUMO unaltered¹².

Simple HMO calculations reveal also an interesting aspect concerning the geometry of compounds of type 2 and 4. It is found (Fig.2) that the bond order between atoms

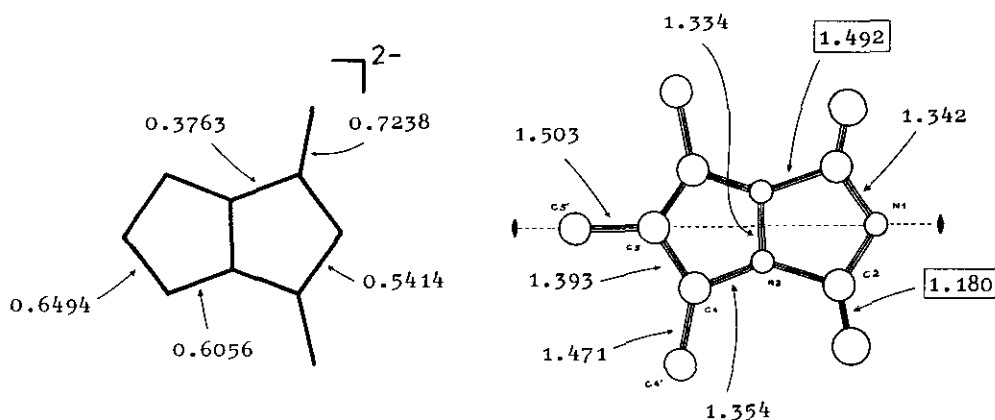


FIG. 2 Bond Orders of 1 (HMO values) and Geometrical Data of 4 (X-ray; bond lengths in Å).

1 and 7 in 1,3-pentalenylenbismethyl dianion (1) is extremely low ($p_{17} = 0.3763$), and it is to be expected that this bond both in 2 and 4 should be extraordinarily long. This prediction has already been substantiated for a derivative of 2¹³, it could also be corroborated by an X-ray analysis of 4 (Fig.2)¹⁴.

Furthermore the unusually short C=O-bond length (1.180 Å) seems to be at variance with a partial single bond character and substantiates our view that compounds of this type should be considered as mesoionic heterocycles.

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11. Analogous alkylations of other mesoionic compounds have been reported earlier: R.N.Hanley, W.D.Ollis, and C.A.Ramsden, J.Chem.Soc.Perkin Trans.1 **1979**, 732.
12. In entirely the same manner the influence of substituents on the UV spectra of compounds of type 2 can be rationalized. These conclusions are in better agreement with experimental data than those given by other authors⁴.
13. See footnote 5 in loc.cit. 3b.
14. Crystal data: Space group $I4_1/a$, $Z=8$, lattice constants: $a = b = 7.729(6)$ Å, $c = 26.739(9)$ Å; $\alpha = \beta = \gamma = 90.0^\circ$.

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