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

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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-Pentacylenbis(methyl dianion (1) is the isoconjugated basis system of a new
class of mesoionic compounds which recently came to light\textsuperscript{2-4}.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {1};
\node (b) at (2,0) {2-};
\node (c) at (4,0) {R};
\node (d) at (4,-2) {R=Alkyl,Aryl};
\end{tikzpicture}
\end{center}
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-dihydroxy pyrazoles with 1,3-dicarbonyl compounds like 2,4-pentanedione or suitable derivatives thereof\(^5\).

In this communication the preparation and structure of an aza-analogue of 2 (5) is described.

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{Si(CH}_3)_3 \\
\end{array}
\xrightarrow{1. \text{ClCONCO, benzene, } 0^\circ\text{C}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{O} \\
\end{array}
\]

1. CICO\textsubscript{2}, benzene, \(0^\circ\text{C}\)
2. chlorobenzene, reflux

Whereas the direct reaction of 3,4,5-trimethyl pyrazole with chlorocarbonyl isocyanate\(^7\) was unsuccessful, treatment of the activated\(^6\) pyrazole \(\text{2}\)\(^9\) with this 1,3-bielectrophile in benzene at \(0^\circ\text{C}\) yields a precipitate, which on heating in chlorobenzene is transformed to \(\text{3}\)\(^{35\%}\) colorless rhombs with \(\text{mp } 161.5-162^\circ\text{C}\); IR(KBr): \(\nu\) \(1715\) (s), \(1725\) (s), \(1801\) (m), \(2927\) \(\text{cm}^{-1}\); UV(CH\textsubscript{3}CN): \(\lambda \) (log \(\varepsilon\)) = \(233\) (4.159), \(238.5\) (4.136), \(247\) (sh, 4.049), \(255.5\) (sh, 3.792), \(288.5\) \(\text{nm}\) (plateau, 2.615); \(^1\text{H-NMR} (\text{CDCl}_3): \delta = 2.06\) (s, 5-CH\(_3\)), 2.57 \(\text{ppm}\) (s, 4-CH\(_3\), 6-CH\(_3\)); \(^{13}\text{C-NMR} (\text{CDCl}_3): \delta = 7.47\) (q), \(9.81\) (q), \(121.86\) (C-5), \(141.55\) (C-4, C-6), \(150.19\) \(\text{ppm}\) (C-1, C-3)). It is of interest to note that the \(^{13}\text{C}-\text{signal of C-4 (C-6) appears in the same region as the corresponding absorption in 3,4,5-trimethylpyrazole}^{10}.\) Compound \(\text{4}\) is moderately stable in air, but is instantaneously hydrolyzed in moist THF to give a quantitative yield of \(\text{5}\). Treatment of \(\text{4}\) with trimethyloxonium tetrafluoroborate yields \(\text{6}\)\(^{11}\)

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{NH}_2 \\
\end{array}
\]

\(\text{5}\)

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{O} \\
\end{array}
\]

\(\text{H}_3\text{C} \\
\text{O} \\
\text{BF}_4^- \\
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{O} \\
\text{H}_3\text{C} \\
\end{array}
\]

\(\text{6}\)

\(84\%\) colorless prisms with \(\text{mp } 153^\circ\text{C}\); IR(KBr): \(1791\) (s), \(1848\) \(\text{cm}^{-1}\) (m); UV(CH\textsubscript{3}CN): \(\lambda \) (log \(\varepsilon\)) = \(233.5\) (4.234), \(235\) (4.233), \(239\) (sh, 4.219), \(250\) (sh, 3.972), \(307\) \(\text{nm}\)
(3,459); \(^1\)H-NMR (CD\(_2\)CN): \(\delta = 2.12\) (s, 5-CH\(_3\)), 2.70 (s, 4-CH\(_3\)), 3.25 ppm (s, N-CH\(_2\)); \(^13\)C-NMR (CD\(_2\)CN): \(\delta = 7.44\) (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 2\(^{-2}\)-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

![HOMO and LUMO of 1,3-Pentalenylbismethyl Dianion](image)

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

2 lowers HOMO but leaves LUMO unaltered\(^{12}\).

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

![Bond Orders of 1 (HMO values) and Geometrical Data of 4 (X-ray; bond lengths in Å)](image)

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-pentalenylbismethyl dianion (1) is extremely low \( p_{17} = 0.3763 \), and it is to be expected that this bond both in \( \mathbf{2} \) and \( \mathbf{4} \) should be extraordinarily long. This prediction has already been substantiated for a derivative of \( \mathbf{13} \), it could also be corroborated by an X-ray analysis of \( \mathbf{4} \) (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 mesionic heterocycles.

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REFERENCES
1. Mesoionic 4ππ-Heterocycles II\(^{2}\).
5. It has been proposed that compounds of type \( \mathbf{2} \) as well as six-membered heteroaromatic 1,4-dipoles\(^{6}\) should be called 'paraisonic compounds'\(^{5,4}\). This nomenclature seems to imply the conception of an extensive charge localization in 'para' (1,4)-positions; whether this view is correct is open to question.
6. For a comprehensive review see: W. Friedrichsen, Th. Kappe, and A. Böttcher, Heterocycles 19, 1083 (1982).
10. \( \mathbf{3a} \), \( \mathbf{3b} \), \( \mathbf{3c} \)-Trimethylpyrazole - \( 13\)C-NMR(CDCl\(_3\)) \( \delta \): 7.41 (q), 10.59 (q), 110.19 (C-4), 141.77 ppm (C-3, C-5).
12. In entirely the same manner the influence of substituents on the UV spectra of compounds of type \( \mathbf{2} \) can be rationalized. These conclusions are in better agreement with experimental data than those given by other authors\(^{4}\).
13. See footnote 5 in loc. cit. \( \mathbf{3b} \).
14. Crystal data: Space group \( \text{I}_4_1_{/a} \), \( Z=8 \), lattice constants: \( a = b = 7.729(6) \) Å, \( c = 26.739(9) \) Å; \( \alpha = \beta = \gamma = 90.0^\circ \).

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