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CONCERNING THE "NOVEL INTRAMOLECULAR HYDROGEN BOND TO A TRANS-SYN,S-CIS FORMAZAN SYSTEM": SOLUTION ISOMERS OF 3-CARBOXYMETHYLTHIO- AND 3-METHOXYCARBONYL-1,5-DIPHENYLFORMAZAN

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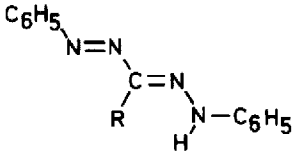
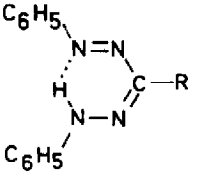
Summary: Spectroscopic studies of the [1,5-$^{15}N_2$]-labelled title compounds demonstrate the presence of the yellow trans-anti,s-trans (1) and the red trans-syn,s-cis (2) isomers in solution. There is no experimental evidence supporting the postulated novel hydrogen bridge 5.

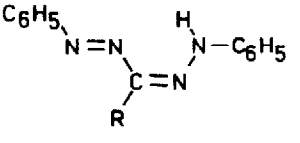
Two isomers of the formazan system can often be observed in solution, the yellow trans-anti,s-trans (1) and the red trans-syn,s-cis form (2) [1,2]. The structure of these isomers has been unequivocally assigned by nmr [3] and ir [4-6] studies. Furthermore in two examples, 3 and 4 [7,8], X-ray structure analysis demonstrated the existence of the trans-syn,s-trans isomer in solid state. Recently, in case of the acid 3 dissolved in chloroform, Irving et al. [7] postulated the formation of a novel intramolecular hydrogen bridge to the trans-syn,s-cis arrangement of the formazan system (5) based on various spectroscopic arguments (nmr, vis, ir). In order to test this idea we prepared



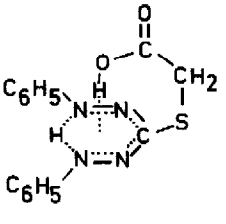
1: trans-anti,s-trans



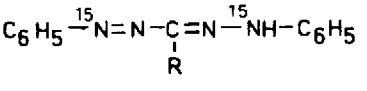
2: trans-syn,s-cis



trans-syn,s-trans	R
3	SCH_2COOH
4	SCH_3



5



	R
6	SCH_2COOCH_3
7	SCH_2COOH

the ^{15}N-labelled formazans 6, m.p. 110 - 111° C, and 7, m.p. 151 - 152° C, by alkylating [9] the corresponding ^{15}N-labelled dithizone with methylbromoacetate or bromoacetic acid and studied some of their spectroscopic properties.

Vis: λ_{max} nm (log ε), 300 K

solvent	6	7
benzene[a]	541 (4.14)	420 (4.31), 538 (3.74)
benzene[b]	413 (4.18), 540 (3.89)	
chloroform[a]	535 (4.15)	418 (4.35), 530 sh (3.68)
chloroform[c]	414 (4.29), 530 (3.77)	
acetone	412 (4.09), 535 (4.02)	414 (4.12), 535 (3.98)
dimethylsulfoxide	429 (3.94), 541 (4.07)	430 (4.04), 547 (3.96)

[a] immediately, [b] equilibrium after 5 d, [c] equilibrium after 4 h

Nmr: δ ppm, ^{15}NH of the isomers in equilibrium, 305 K

solvent	6	7
C_6D_6	9.85 (t, $J_{^{15}NH}$ = 47.5 Hz, ~45%)	not observed
	10.06 (d, $J_{^{15}NH}$ = 94 Hz, ~55%)	not observed
$CDCl_3$	10.21 (t, $J_{^{15}NH}$ = 47 Hz, ~40%)	not observed
	9.93 (d, $J_{^{15}NH}$ = 93.5 Hz, ~60%)	not observed
$(CD_3)_2CO$	11.14 (t, $J_{^{15}NH}$ = 48 Hz, ~70%)	11.15 (t, $J_{^{15}NH}$ = 48 Hz)[10]
	10.29 (d, $J_{^{15}NH}$ = 94.5 Hz, ~30%)	not observed
$(CD_3)_2SO$	11.60 (t, $J_{^{15}NH}$ = 48.5 Hz, ~75%)	11.58 (t, $J_{^{15}NH}$ = 48.5 Hz, ~70%)
	10.83 (d, $J_{^{15}NH}$ = 96 Hz, ~25%)	10.82 (d, $J_{^{15}NH}$ = 93 Hz, ~30%)

Ir: $\nu\,^{15}NH$ cm^{-1}, rel. intensity

	6	7
chloroform[a]	3334 ≫ 3246	3333 < 3239
chloroform[b]	3334 < 3246	
carbon tetrachloride[b] ($5 \cdot 10^{-5}$ M, l = 10 cm)	3339 < 3240	3340 < 3243

[a] immediately, [b] equilibrium after 4 h

Direct spectroscopic observation of the ester 6 in benzene (λ_{max} = 541 nm, δ = 9.85 ppm (t), $\nu\,^{15}NH$ 3330 cm^{-1}) shows the presence of only the red trans-

syn,s-cis form 2, since the ^{15}NH nmr triplet originates from a fast intramolecular proton exchange between the terminal ^{15}N atoms with respect to the nmr time scale. After some time this red form is partly (~60%) converted to a yellow trans-anti form (λ_{max_1} = 413 nm, δ = 10.06 ppm (d), ν^{15}NH 3240 cm^{-1}). The position of this νNH is not affected in dilution experiments (CCl_4, $5 \cdot 10^{-5}$ M/l) indicating another intramolecular hydrogen bridge. Since the νC=O 1730 cm^{-1} of 6 remains unchanged during the isomer conversion, the hydrogen bridge is apparently directed to the S atom [11] in agreement with a trans-anti,s-trans arrangement (1) in the yellow isomer. The equilibrium between the red (2) and the yellow form (1) is solvent dependent. According to this vis and nmr data the yellow form is slightly preferred in unpolar solvents, whereas in polar solvents the red form dominates. These findings do not agree with results of other formazans, e.g. 3-ethyl-1,5-diphenylformazan [2], with which an opposite isomer distribution has been observed. In this case the preferred formation of the red form 2 in unpolar solvents was attributed to the intramolecular hydrogen bridge, the cleavage of which is facilitated by polar solvents. The isomer distribution of 6 and 7, however, can hardly be associated directly with the strength of the hydrogen bridges being considered (N-H··N versus N-H···S) in the formazan isomers. The ratio of the isomers of 6 and 7 in different solvents is probably influenced by various factors, e.g. solvatation, steric effects, hydrogen bridge, etc..

The isomer conversion of formazans is catalyzed by acid or base. Therefore in solution the acid 7 shows immediately the equilibrium distribution of the isomers. Comparing the vis and ir (ν^{15}NH) results [14] of 6 and 7 one sees no significant differences between both compounds. As with the ester 6 the drastic changes in the vis spectra of the acid 7, going from acetone to chloroform, are due to the conversion of a large part of the red trans-syn,s-cis form (2) into the yellow trans-anti,s-trans form (1). The nmr data of the acid 7 in dimethylsulfoxide agree well with those of the ester 6 in this solvent. In acetone, however, the acid 7 shows only the NH-signal (δ = 11.15 ppm, t [10]) of the trans-syn,s-cis form at 305 K. The NH signal of the yellow trans-anti form is not observed, apparently due to a proton exchange within the nmr time scale. This exchange can also be seen in the nmr spectra of the ester 6 and the acid 7 in dimethylsulfoxide; with higher temperature the NH signal of the yellow trans-anti form (δ = 10.83 ppm, d) becomes increasingly broadened. Nmr spectra of the acid 7 in chloroform or benzene at 305 K show no NH signals and the CH resonances are represented by broad lines, again indicating an exchange in 7 under these conditions. So the "coalescence" [7] of the methylene proton resonances of the acid 7 in acetone: δ = 3.79 ppm (~30%), 3.90 (~70%); acetone/chloroform (1:2): δ = 3.70 ppm (~60%), 3.86 (~40%), into the broad CH_2 signal, δ = 3.68 ppm, in chloroform is obviously the result of proton exchange and/or isomer conversion in this system within the nmr time

scale. This is additionally supported by nmr spectra of 7 in $CDCl_2CDCl_2$; the broad CH-resonance lines at room temperature sharpen at 400 K to give δ = 3.70 ppm (s, 2 H, CH_2), 7.24 (broad t, 2 H, H_p), 7.42 (t, J ≈ 7 Hz, 4 H, H_m), 7.56 (broad d, 4 H, H_o).

All spectroscopic results of 6 and 7 presented here and also all observations of 3 [7] can be traced back to the presence of the known yellow (1) and red (2) formazan isomers. Many properties of the acid 7 (vis, ir) correspond to those of the ester 6, which is not capable of forming a hydrogen bridge of type 5. The coalescence of the methylene proton signals of 7 in chloroform is due to a fast proton exchange and isomer conversion, obviously caused by the catalytic activity of the carboxylic function.

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10 Originally [7] erroneously assigned to the carboxylic proton.

11 Comparable N-H···S hydrogen bridges are present in molecules of primary dithizonates: νNH 3280 cm^{-1} (CCl_4) [12], and in the yellow trans-anti,s-trans isomer of 4: νNH 3252 cm^{-1} (CCl_4) [13].

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14 All quoted ir data are taken from solution spectra. In KI or paraffin also 6 and 7 show a weak $\nu^{15}NH$ absorption at ~3330 cm^{-1}; this band, however, cannot be definitely assigned to the isomer structure 3 or 2.

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