Novel Intramolecular Hydrogen Bond to a Quasi-aromatic Formazan Ring: Solution Conformation and *X*-Ray Crystal Structure of 3-Carboxymethylthio-1,5-diphenylformazan

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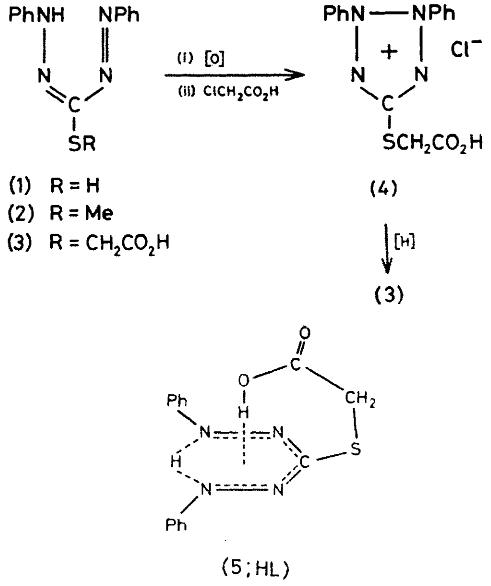
Summary Although the *X*-ray structure of 3-carboxymethylthio-1,5-diphenylformazan (**3**) shows the existence of intermolecularly hydrogen bonded dimers in the solid state, physical properties of chloroform solutions indicate its existence as a monomer with a novel intramolecular hydrogen bond to a quasi-aromatic formazan ring system.

The title compound (**3**), currently being studied as an analytical reagent derived from dithizone (**1**), was prepared[1] according to the Scheme. When dissolved in $CHCl_3$ or in Me_2CO the formazan (**3**) was shown to be monomeric by isopiestic measurements against azobenzene.[2] The values of the acid dissociation constants (spectrophotometric, $I = 0{\cdot}1$ M KCl, 25 °C) $K_1 = [H^+][HL]/[H_2L^+] = 10^{+0{\cdot}36}$ and $K_2 = [H^+][L^-]/[HL] = 10^{-12{\cdot}48}$ show that the formazan (**3**;HL) is a very weak base and an unexpectedly weak acid. Furthermore, neither the carboxylic nor the imino hydrogen atom is observed in ^1H n.m.r. measurements made in chloroform [δ ($CDCl_3$, Me_4Si, 90 MHz) 3·68 (s, 2H, CH_2) and 7·17—7·76 (m, 10H, ArH)], while in acetone {δ [$(CD_3)_2CO$] 3·80, 3·90 (s, s, 2H, CH_2), 7·10—7·84 (m, 10H, ArH), and 11·22 (s, 1H, CO_2H, disappears on addition of D_2O)} the carboxylic proton is unambiguously present. Progressive dilution of an acetone solution with $CDCl_3$ results in the disappearance of the carboxylic proton resonance and coalescence of the two methylene resonances to give the $CDCl_3$ spectrum. In the visible spectrum there is a concomitant disappearance of a peak at 540 nm and increase in absorbance of that at 420 nm, with an isosbestic point at 475 nm. However, titration with $(CD_3)_2SO$ leaves the methylene resonances unchanged but shifts the CO_2H resonance progressively downfield with unchanged integral. The latter effect is ascribed to interaction of the carboxylic proton with the more polar $(CD_3)_2SO$ molecules, while in $CDCl_3$ a conformation may be proposed in which the carboxylic proton appears in a somewhat unusual environment.

Electron delocalisation in the formazan ring, previously attributed to mesomerism resulting from internal hydrogen bonding,[3] would now seem to be more correctly explained by the very rapid tautomerism which has been established by n.m.r. studies using ^{15}N-labelled formazans.[4] This produces an equivalent effect in which $4n + 2$ π-electrons are delocalised to yield a quasi-aromatic formazan ring in which C and N atoms are all sp^2-hybridised. Scale models show that the carboxylic proton of the formazan (**3**) could itself be intramolecularly hydrogen-bonded to any one of the four N atoms and that the arrangement most favoured sterically is that in which the –OH group of the side chain $-SCH_2CO_2H$ points almost axially through the centre of the π-electron system of the formazan ring [as (**5**)]. The loss of resonance stabilization energy consequent on dissociation of the carboxylic proton could then well explain the relative stability of the form HL compared with H_2L^+ and L^- and hence the low value of pK_1 and high value of pK_2. Clearly similar stabilisation by intramolecular hydrogen bonding to a π-electron system is not possible for the corresponding tetrazolium chloride (**4**; $pK_a = 2{\cdot}75$, potentiometric, $I = 0{\cdot}1$ M KCl, 25 °C) where a positive charge contribution exists on the meso-ionic ring, whence the increased acidity of the salt (**4**).



SCHEME

Poor solubility has so far precluded satisfactory i.r. solution spectra, but a broad solid state i.r. band in the region 2500—3000 cm^{-1} points to a strongly hydrogen bonded OH group, while lack of any absorption in the region 3100—3500 cm^{-1} indicates the absence of a free :NH group and implies its participation in strong hydrogen bonding. This observation favours structure (**5**), as does the fact that in spite of many varied attempted methods of preparation, no metal complexes of (**3**) have yet been isolated.

Although hydrogen bonding to π-electron systems is well established[5] there are few precedents[6] for the structure (**5**) and an *X*-ray crystallographic investigation of the compound (**3**) seemed necessary to ascertain whether this

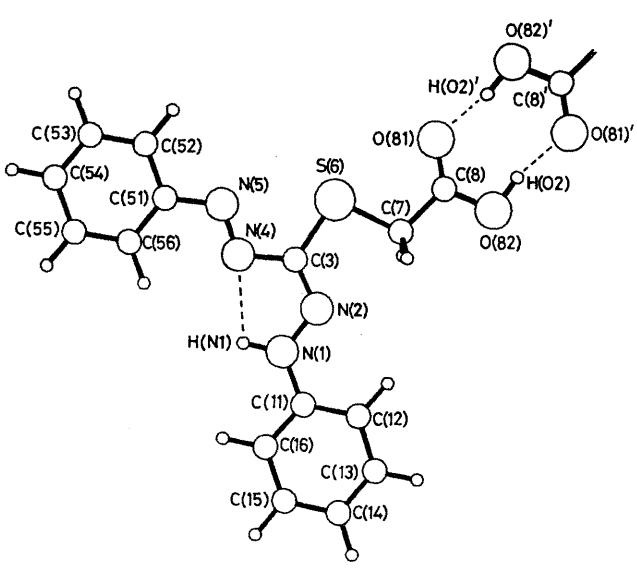


FIGURE. The molecular geometry of the formazan (3), showing a portion of the symmetry related group of the dimer. The dashed lines indicate hydrogen bonds. Selected bond lengths: C(11)–N(1), 1·398(6); N(1)–N(2), 1·352(6); N(2)–C(3), 1·312(6); C(3)–N(4), 1·407(6); N(4)–N(5), 1·273(5); N(5)–C(51), 1·417(6); C(3)–S(6), 1·757(5); S(6)–C(7), 1·800(5); C(7)–C(8), 1·491(7); C(8)–O(81), 1·219(6); and C(8)–O(82), 1·328(6) Å.

molecular structure persisted in the solid state. In fact this proved not to be the case for in the solid state the formazan crystallizes as a dimer (Figure). Crystals of (**3**) are monoclinic with $a = 27{\cdot}98(1)$, $b = 10{\cdot}127(5)$, $c = 5{\cdot}208(3)$ Å, $\beta = 91{\cdot}59(5)^\circ$, space group $P2_1/n$, $Z = 4$. The structure was solved by the automatic centrosymmetric routine of the SHELX[7] program system from data collected by the ω–2θ scan technique in the range $3^\circ \leqslant \theta \leqslant 20^\circ$ on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Refinement by full-matrix least-squares gave $R = 0{\cdot}053$ for 975 observed reflections with $I_{\text{rel}} > 2\sigma I_{\text{rel}}$.‡ Molecules of the formazan (**3**; Figure) are remarkably planar and are strongly hydrogen bonded through their carboxylic groups to form dimers [O(82) · · · O(81)′ distance 2·67 Å]. The two phenyl rings are twisted slightly out of the mean plane of the molecule in opposite senses, the angle between the normal to each phenyl ring plane being 11·8°. As found for *S*-methyldithizone (**2**),[8] the imino proton is intramolecularly hydrogen-bonded to N(4) effectively locking the molecule in a *syn*, *s-trans* configuration. For a constrained N–H distance of 1·00 Å, the distance H(N1) · · · · N(4) is 2·16 Å. Several contacts less than the sum of the van der Waals radii exist between planes of dimers in the crystal, contributing to its low solubility.

We thank the C.S.I.R. and the University of Cape Town for financial assistance.

(*Received*, *3rd August* 1978; *Com.* 854.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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