X-Ray Crystallographic and Spectroscopic Study of the Configurations of Isomeric 3-Methylthio-1,5-diarylformazans and their Interconversion in Solution

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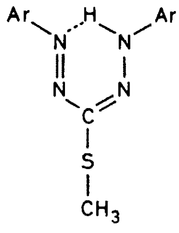
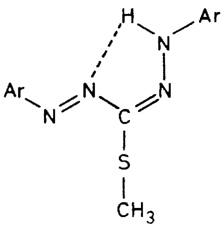
Summary ^{1}H N.m.r. and i.r. spectroscopic studies on solutions of Ar.N:N.C(SR):N.NH.Ar (Ar = Ph, *p*-tolyl, or *o*-tolyl; R = CH_3 or CD_3) taken in conjunction with *X*-ray crystal structures of pure isomers have made it possible to establish the structural causes for temporal changes in the visible spectra.

FRESH solutions of 3-methylthio-1,5-diphenylformazan (**1**) in, *e.g.*, chloroform, are permanganate pink, with well defined bands at 270 and 550 nm (ϵ_{550} 1225 m^2 mol^{-1}). On standing in the dark at room temperature the colour changes to yellow and the spectrum then shows bands at 280, 420, and 540 nm (ϵ_{420} 1775 m^2 mol^{-1}), the band originally at 550 nm becoming less intense as the new band appears at 420 nm. The process is kinetically first order, and is greatly accelerated by traces of acids and alkalis. The isomerization is reversed on illumination.[1] Analogous effects appear with a number of formazans[2,3] and *S*-alkylated dithizones in general.[4] On concentration of solutions of (**1**) (whether in the pink or yellow form) only the magenta-red solid (diffuse reflectance spectrum, d.r.s.: λ_{max} 550 nm) is deposited. *X*-Ray crystallography[5] shows that the whole molecule is effectively planar and its *syn*,s-*trans* configuration[†] can be represented by structure (**1b**).

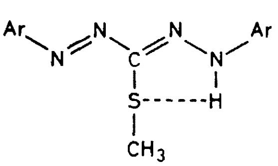
[†] Ignoring isomers which are unlikely to occur owing to serious steric crowding (*i.e.*, all the *cis*-configurations relative to the N=N double bond) leaves four isomers (**a**—**d**) as a result of *syn–anti* isomerization about the C=N double bond and isomerization about the C–N single bond (designated s-*cis* and s-*trans*).



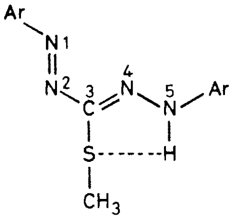
(a) *syn*,s–*cis*



(b) *syn*,s - *trans*



(c) *anti*,s– *trans*



(d) *anti*,s-*cis*

(**1**) Ar = Ph
(**2**) Ar = *p*-tolyl
(**3**) Ar = *o*-tolyl

The di-(*p*-tolyl) (**2**) and di-(*o*-tolyl) (**3**) homologues of (**1**) and the corresponding $-SCD_3$ analogues have been prepared[6] Red needles of (**2**) dissolve in chloroform to give a pink solution (λ_{max} 550 nm, ϵ 1406 m^2 mol^{-1}) which slowly turns brownish to give a new band at 425 nm with a concomitant decrease in the absorbance at longer wavelength, in exact analogy with the behaviour of (**1**) Presumably (**2**) has the same solid state configuration (d r s λ_{max} 550 nm) as (**1**), *viz* *syn*,s-*trans* (**2b**) The compound (**3**), however, crystallizes as yellow plates (d r s λ_{max} 423 nm) and the *X*-ray structural analysis‡ establishes an *anti*,*s-trans* configuration [as (**3c**)] During several days in the dark the initially yellow solution of (**3c**) in chloroform (λ_{max} 420 nm, ϵ 2936 m^2 mol^{-1}) slowly formed a brown equilibrium mixture (isosbestic point 485 nm) with a pink isomer (**3b**) having a peak at 560 nm Under the same conditions the initially pink (**2b**) reaches equilibrium with the yellow isomer (**2c**)

The ^{1}H n m r spectrum of a freshly prepared (pink) solution of (**2**) in $CDCl_3$ shows a single resonance (6H) for the two equivalent *p*-tolyl Me groups Although this would be consistent with structure (**2a**), formazans known to have this structure in the solid state[7] show an imino proton at δ ($CDCl_3$, Me_4Si) 14—16 and ν (N–H) *ca* 3030 cm^{-1} in fresh solutions Spectroscopic data for (**1**), (**2**), and (**3**) do not provide evidence for such strong hydrogen bonding (Table) and configuration (**2b**) [already shown to exist in crystals of (**1**)][5] should be considered, the equivalence of the two Me groups being achieved by interconversion, fast on the n m.r time scale, between two equivalent forms of (**2b**) by rotation about the C–N single bond (*trans* → *cis*) to give the quasi-aromatic *syn*,s-*cis* structure (**2a**) as an intermediate § During the slow isomerization of pink (**2a**) to yellow (**2c**) two new *p*-tolyl Me resonances develop until after 3 days in the dark three lines are found, still integrating *in toto* for 6H The new resonances are attributed to the magnetically non-equivalent *p*-tolyl Me groups of isomer (**2c**) produced by a *syn* → *anti* isomerization structure (**2d**) is less favoured owing to repulsion of the lone pairs on nitrogens 1 and 4 The magnetically non-equivalent *o*-tolyl Me groups in a fresh (yellow) solution of (**3**) show two resonances of equal intensity derived from form (**3c**), as expected from the *X*-ray analysis of the yellow crystals of (**3**) On standing in the dark isomerization about the C=N bond occurs yielding the pink *syn*,s-*cis* (**3a**) tautomeric pair which gives rise to an additional *o*-tolyl Me resonance in the spectrum of the equilibrium mixture During the isomerization (**2a**) → (**2c**) a new *S*-Me resonance appears at virtually the same chemical shift value as that given by a fresh solution of (**3c**), (**3c**) → (**3a**) gives a new *S*-Me line corresponding to a fresh solution of (**2a**) (Table) The equilibrium mixture in either case contains roughly equal proportions of the two isomers to give very similar ^{1}H n m r spectra, contrasting mainly in the difference in chemical shifts of the two *o*-tolyl Me resonances (**3c**, *e g* ,

TABLE ^{1}H Chemical shift values (p p m) of imino and methyl resonances at ambient temperature [$\delta(CDCl_3)$ and, in parentheses $\delta(C_6D_6)$, Me_4Si 100 MHz] ν(N–H)/cm^{-1} for KBr pressed disks and CCl_4 solutions

		Solid	Fresh solution		Equilibrium mixture after 70 h	
(**1**)	$-NH$		10 26	(10 02)	10 26	(10 02)
					9 46	(9 24)
	$-SCH_3$		2 54^a	(2 29)^a	2 54^a	(2 29)^a
					2 40^a	(1 92)^a
	ν(N–H)	3338	3342		3342	3253
(**2**)	$-NH$		10 22	(10 06)	10 19	(10 06)
					9 43	(9 26)
	$-SCH_3$		2 52^a	(2 32)^a	2 52^a	(2 32)^a
					2 39^{a,b}	(1 95)^a
	$ArCH_3$		2 39	(2 09)	2 39	(2 09)
					2 42	(2 09)^b
					2 34	(2 03)
	ν(N–H)	3341	3344		3344	3254
	$-NH$		9 53	(9 41)	9 52	(9 41)
					10 28	(10 21)
	$-SCH_3$		2 43^a	(1 95)^a	2 43^a	(1 95)^a
					2 51^a	(2 35)^a
	$ArCH_3$		2 40	(1 98)	2 40	(1 98)
			2 72	(2 69)	2 72	(2 69)
					2 53	(2 29)
	ν(N–H)	3270	3269		3269	3361

[a] Resonance disappears in spectrum of $-SCD_3$ analogue
[b] Apparent from peak integration

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‡ *Crystal data* (**3**), $C_{16}H_{18}N_4S$, M_r = 298 40, monoclinic, space group $P2_1/n$, a = 7 993(4) b = 20 910(9) c = 10 154(5) Å, β = 110 43(5)°, U = 1590(1) Å^3, D_m = 1 29 (by flotation), D_c = 1 25 g cm^{-3} Z = 4, $F(000)$ = 632 The structure was solved by direct methods using the SHELX-76 program system (G M Sheldrick, Cambridge) from data collected by the ω—2θ scan technique in the range $3 \leqslant \theta \leqslant 20°$ on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation [λ = 0 7107 Å μ(Mo-K_α) = 1 63 cm^{-1}] Refinement by full-matrix least-squares gave R = 0 064 for 1319 observed reflections with $I_{rel} > 2\sigma I_{rel}$ 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

§ *Added in proof* However, the ^{13}C n m r spectrum of (**2**) and the n m r spectrum of the compound labelled at N 1 and N-5 with ^{15}N provide unambiguous support for structure (**2a**). Details will be reported in the full paper

C_6D_6 0·71 p.p.m.) compared with those of *p*-tolyl in the same configuration (**2c**; 0·06 p.p.m.), presumably owing to the magnetic anisotropy effect of the azo-group on one of the *o*-tolyl Me groups. The approach to an equilibrium mixture starting from either the *syn*,s-*cis* (**2a**) or the *anti*,s-*trans* (**3c**) isomer can be followed by observing the change in ν (N–H) since the intramolecular N–H · · · N and N–H · · · S hydrogen bonds differ significantly in strength with Δν (N–H) *ca.* 90 cm^{-1} (Table). Changes in the imino proton resonance (Table) also reflect this difference in internal hydrogen bonding.

Several authors have speculated on the nature of the pink and yellow isomers of (**1**)[4,6,8,9] and, indeed, of formazans in general.[2,3,10] Our results explain the isomerism occurring in (**1**) and may be applied to that found in many other formazans. They lead us to reject the assignments proposed by Burns and Duncan[9] but they support the speculative configurations proposed by Kuhn and Weitz.[3]

We thank Dr. K. R. Koch for helpful discussions, the C.S.I.R. (Pretoria) and the University of Cape Town for research grants, and the C.S.I.R. for the collection of diffractometer data.

(*Received*, 28*th April* 1980; *Com.* 439.)

[1] H. M. N. H. Irving, 'Dithizone,' Analytical Sciences Monographs No. 5, The Chemical Society, London, 1977, p. 84.
[2] I. Hausser, D. Jerchel, and R. Kuhn, *Chem. Ber.*, 1949, **82**, 515; W. Otting and F. A. Neugebauer, *Z. Naturforsch., Teil B*, 1968, **23**, 1064; *Chem. Ber.*, 1969, **102**, 2520.
[3] R. Kuhn and H. M. Weitz, *Chem. Ber.*, 1953, **86**, 1199.
[4] P. S. Pel'kis and R. G. Dubenko, *Dokl. Akad. Nauk SSSR*, 1956, **110**, 798; *Ukr. Khim. Zh.* (*Russ. Ed.*), 1957, **23**, 64, 69.
[5] J. Preuss and A. Gieren, *Acta Crystallogr., Sect. B*, 1975, **31**, 1276.
[6] H. Irving and C. F. Bell, *J. Chem. Soc.*, 1954, 4253; A. H. Nabilsi, Ph.D. Thesis, University of Leeds, 1972.
[7] E. Dijkstra, A. T. Hutton, and L. R. Nassimbeni, submitted for publication in *Acta Crystallogr.* It is shown that 3-nitro-1,5-di(2,6-dimethylphenyl)formazan adopts this quasi-aromatic structure in the solid state.
[8] W. Ferguson, B.Sc. Thesis, University of Oxford, 1957; C. H. Carlin, Ph.D. Thesis, The Johns Hopkins University, Baltimore, 1966.
[9] G. R. Burns and J. F. Duncan, *Chem Commun.*, 1966, 116.
[10] A. W. Nineham, *Chem. Rev.*, 1955, **55**, 355; G V. D. Tiers, S. Plovan, and S. Searles, Jr., *J. Org. Chem.*, 1960, **25**, 285, C. Schiele, K. Halfar, and G. Arnold, *Tetrahedron*, 1967, **23**, 2693; P. B. Fischer, B. L. Kaul, and H. Zollinger, *Helv. Chim. Acta*, 1968, **51**, 1449; L. Mester, A. Stephen, and J. Parello, *Tetrahedron Lett.*, 1968, 4119; G. Arnold and C. Schiele, *Spectrochim. Acta, Part A*, 1969, **25**, 685.