# New Evidence for the Structure of Dithizone in Solution from ¹H and ¹³C N.M.R. Spectra and ¹⁵N-Labelling

By ALAN T. HUTTON and HARRY M. N. H. IRVING*
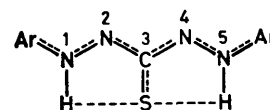
(*Department of Analytical Science, University of Cape Town, Rondebosch 7700, South Africa*)

*Summary* ¹H N.m.r. spectra of dithizone, its ¹⁵N-labelled analogue, and its alkyl-substituted homologues, as well as the ¹³C n.m.r. spectrum, suggest that dithizone should be regarded as a single species in solution rather than as the tautomeric equilibrium of thiol and thione forms which has been widely accepted.

THE structure of the analytical reagent dithizone in the solid state has been unequivocally established as (1a) by X-ray crystallography.[1] However, the existence of two strong bands in the visible spectrum of solutions in organic solvents has long been interpreted as due to thiol and thione tautomers, $PhN:N \cdot C(SH):N \cdot NHPh \rightleftharpoons PhN:N \cdot CS \cdot NH \cdot NHPh$, respectively. Although the wavelength of the absorption bands does not vary greatly with change of solvent, their relative intensity does and a number of correlations have been noted, *e.g.*, between the peak height ratio, $R =$ (absorbance at long wavelength maximum)/(absorbance at short wavelength maximum), and the concentration ratio [keto]/[enol] for ethyl acetoacetate in the same solvent, or between values of $R$ for a series of structurally modified dithizones and the Hammett factors of the substituents.[2]

The application of n.m.r. spectroscopy has hitherto been indecisive owing to the low solubility of dithizone but Coleman *et al.*, using the more soluble homologue (1b), concluded that solutions in $CDCl_3$ contained only one symmetrical species (as 1), although their signal at $\delta$ 12·03 p.p.m. integrated for only 1·6 imino protons.[3] Nabilsi reported an additional signal from (1a) at $\delta$ 0·97 which with that at $\delta$ 12·61 integrated to exactly 2 protons. He attributed

the high-field signal to an SH group in the absence of significant hydrogen bonding and concluded that the solution comprised a tautomeric mixture of (1a) and a thiol form in the approximate ratio 3 : 1.[4]



(1)　a; Ar = Ph
　　　b; Ar = $o$-EtC₆H₄

Although the use of Fourier transform n.m.r. spectroscopy facilitates measurements on sparingly soluble solutes it must not be overlooked that residual protons in deuteriated solvents can give rise to enhanced signals; a residual line from adventitious $CHCl_3$ enhances the integrated value for aromatic protons so that the intensity of other lines relative to this will be underestimated. In the present work alkyl-substituted dithizones were used to provide well defined lines for integration reference and to examine the equivalence or otherwise of the two aryl groups. Nabilsi's alleged peak at $\delta$ 0·97 could not be reproduced and may have originated from solvent impurity or even a spinning side-band of an intense $Me_4Si$ resonance. We have recorded ¹H Fourier transform n.m.r. spectra for dithizone and several alkyl-substituted homologues in $CDCl_3$, $(CD_3)_2CO$, and $C_6D_6$. In every case the substituent alkyl groups (and hence the two

aromatic rings) are found to be exactly equivalent on the n.m.r. time-scale, and spectra at $-50$ °C differed from those at $+60$ °C only by the expected slight narrowing of peaks. Furthermore the NH singlet at $ca.$ $\delta$ 12·6 always integrated *exactly* for 2 protons and disappeared immediately and completely on washing with $D_2O$.

Solutions of dithizone in organic solvents thus appear to contain a single species which can be formulated as (1a). The two non-aromatic protons must be bound to equivalent nitrogen atoms $N(1)$ and $N(5)$, for in the $^1H$ n.m.r. spectrum of dithizone labelled with 96 atom-% $^{15}N$ in both these positions the NH resonance is split into a doublet with a normal coupling constant value of 90·8 Hz; the value $^1J(^{15}N-H) = 92·2$ Hz has been found for the yellow *anti*, s-*trans* form of $S$-methyldithizone, where tautomerism is impossible.[5] If tautomerism were to occur the normal $^{15}N-$H coupling constant value would be approximately halved, *e.g.*, in the case of the pink *syn*,s-*cis* form of $S$-methyldithizone (47·6 Hz).[5]

Further evidence is provided by the $^{13}C$ n.m.r. spectrum of dithizone labelled at $C(3)$ by a synthesis from 91 atom-% $^{13}CS_2$.[5] Only a single sharp line at $\delta$ ($CDCl_3$) 171·4 p.p.m. downfield from $Me_4Si$ occurs in the broad-band $^1H$-decoupled spectrum, and in the $^1H$-coupled spectrum this becomes a perfect 1:2:1 triplet with $^3J(^{13}C-N-N-H) = 6·0$ Hz (unchanged at $-50$ °C) which collapses to a singlet on washing with $D_2O$. The same coupling $^3J(H-N-N-^{13}C) = 6·0$ Hz (doublet) is found in the $^1H$ n.m.r. spectrum of $^{13}C$-labelled dithizone.

Support for the view that solutions of dithizone in organic solvents comprise only a single species with two well defined absorption bands in the visible region may be found in the i.r. measurements of Kemula *et al.*[6] and from the theoretical calculations of energy and intensity of electron transitions (by LCAO MO SCF and LCI methods) on a model almost identical with (1a). For this Spěváček and Spěváčková predict a species with two bands in its visible spectrum, one at $ca.$ 800 nm and a second more intense band at $ca.$ 430 nm.[7] This agreement with experiment for the band at the shorter wavelength is satisfactory, for $\lambda_{max}$ ranges from 440 to 462 nm according to the solvent. However the band at the higher wavelength occurs experimentally at 600—640 nm and *this* band is invariably the more intense.

[1] P. A. Alsop, Ph.D. Thesis, University of London, 1971; M. Laing, *J. Chem. Soc., Perkin Trans.* 2, 1977, 1248.
[2] For a full discussion and references see H. M. N. H. Irving, 'Dithizone,' Analytical Sciences Monographs No. 5, The Chemical Society, London, 1977.
[3] R. A. Coleman, W. H. Foster, J. Kazan, and M. Mason, *J. Org. Chem.*, 1970, **35**, 2039.
[4] A. H. Nabilsi, Ph.D. Thesis, University of Leeds, 1972.
[5] A. T. Hutton and H. M. N. H. Irving, unpublished data; *cf.* A. T. Hutton, Ph.D. Thesis, University of Cape Town, 1980.
[6] W. Kemula, T. Gańko, and A. Janowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1971, **19**, 325.
[7] V. Spěváček and V. Spěváčková, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1299.