Tetrahedron Letters, Vol.22, No.40, pp 4037 - 4040, 1981
Printed in Great Britain

0040-4039/81/404037-04$02.00/0

ON THE STRUCTURE OF NITROFORMAZANS

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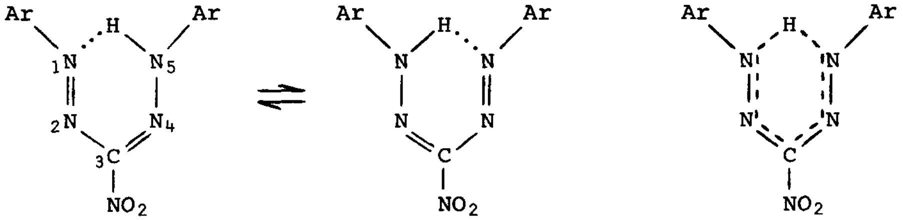
Summary: A *syn*,s-*cis* structure, best described as mesomeric, is proposed for a series of symmetrical nitroformazans, based on the *X*-ray crystal structure of 3-nitro-1,5-di(2,6-dimethylphenyl)formazan. Spectroscopic measurements, however, do not exclude the possibility of rapid tautomerism in solution.

X-Ray crystallographic investigations of formazans have yielded examples of both *syn*,s-*trans*[2] and *anti*,s-*trans*[3] configurations relative to the formal double C=N and single C-N bonds, but no instance of the closed ring *syn*,s-*cis* isomer (as 1) has been reported, although this configuration is adopted when some formazans coordinate with metal ions to form chelate complexes,[4] and in crystals of the hydrochloride of 5-[bis(phenylazo)methylene]-1,3-diphenyltetrazoline betaine.[5] Nineham[6] summarized evidence to show that the structure of the red formazans in solution could be represented by a rapid tautomeric equilibrium between the two cyclic hydrogen-bridged *syn*,s-*cis* structures 1a ⇌ 1b, and this classical viewpoint has received support from i.r.[7] and n.m.r.[8] spectral work.



1a 1b 2

We have found that the red 3-nitro-1,5-di(2,6-dimethylphenyl)formazan crystallizes[9] in the formal *syn*,*s*-*cis* configuration and that the structure may best be represented by the mesomeric structure (2, Ar = 2,6-dimethylphenyl). The bond lengths[10] reveal extensive delocalization of π electrons within the N-N-C-N-N chain, which itself is planar to within ±0.02 Å. The two N-N distances are identical, with bond orders[11] of 1.58, while the two C-N distances within the formazan ring show bond orders of 1.47 and 1.62. A difference Fourier synthesis using all atoms except the imino H in the calculation located this atom as a sharp peak midway between N(1) and N(5) completing a hexagonal formazan ring. The imino proton was therefore constrained to be equidistant from N(1) and N(5) and its temperature factor was refined independently to U =

0.25(4) Å^2, with an N•••H distance of 1.50(8) Å. The refinement converged to R = 0.059. It was considered possible, however, that the single peak found for the imino proton could have resulted from the sum of two smaller peaks derived from half-hydrogens on each terminal N atom. The final refinement was therefore repeated and the single proton previously constrained to be equidistant from N(1) and N(5) was replaced by two half-hydrogens each fixed at 1.08 Å from the parent N atom in sp^2 geometry. The site occupancy factors (s.o.f.'s) were tied together and refined so that their sum was always unity. After the same number of full-matrix least-squares refinement as used in the initial model the isotropic temperature factor for the half-hydrogens H(N1) and H(N5) (refined as a single parameter) dropped to 0.11(3) Å^2 with s.o.f.'s of 0.55(7) and 0.45(7), respectively. R increased slightly to 0.063. Besides providing a physically reasonable N-H distance, this model results in a significantly lower temperature factor for the imino proton, while the slight increase in R can be shown by the Hamilton R-factor test to be insignificant.[12] This model was therefore chosen to be reported, though the bond lengths and angles are, within the e.s.d.'s, the same for both models.

While it is not unequivocally established that there are two equivalent proton positions rather than a single average one, the results do clearly suggest that the barrier in the potential function for movement of the proton must be relatively low, and the function itself nearly symmetrical. Lundgren and Olovsson[13] have pointed out that it is practically impossible to differentiate, on the basis of diffraction data alone, between two overlapping disordered hydrogen peaks and a truly single central peak. In spite of the equivalence of chemical bonds which would be distinct in individual tautomers, the co-existence of two separate tautomers in this crystal (*i.e.*, static disorder) seems unlikely in view of the normal values for the anisotropic thermal motion parameters which give no evidence of the high apparent tangential motion of the atoms in the formazan ring which such a disorder would simulate. The simplest interpretation of this structure is to consider it as the superimposition of two equivalent resonance forms, corresponding to (1a, Ar = 2,6-dimethylphenyl) and the equivalent form (1b) with the double bonds all shifted to the neighbouring position and the bond from N to H transferred to the other terminal N atom. This view would lead one to expect the formazan ring C-N and N-N bonds to correspond to the aromatic distance, which indeed they do. This then constitutes a mesomeric structure, best represented by (2, Ar = 2,6-dimethylphenyl), derived as a resonance hybrid (in valence-bond terminology) of two limiting forms. In molecular-orbital parlance the system would be described as 'electron-delocalized'. In this description the precise location of the imino proton is not important and it need simply be considered as being somewhere between N(1) and N(5) with a relatively low barrier in the potential function.

The similarity of the diffuse reflectance spectra and the solid state i.r. spectra through the series of nitroformazans (1, Ar = phenyl, *p*-, *m*-, or *o*-tolyl, 3,5- or 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, *p*-isopropylphenyl, or *p*-n-butylphenyl) indicates that the structure determined here by *X*-ray analysis may be assigned to all the members of this series. The ν(N-H) vibration is not observed[14] in either the solid state or in CCl_4 solution spectra, possibly being masked by ν(C-H) vibrations. The postulated *anti*,s-*cis* configuration of the nitroformazans in solution[15] seems unlikely since this would imply hydrogen bonding between the imino proton and the nitro group whereas the NO_2 stretching frequencies in the series (around 1540 and 1355 cm^{-1}, KBr pressed disks) do not change in CCl_4 solution spectra. In addition, the $\lambda_{max.}$ values in the visible spectra of chloroform solutions, which are in themselves very similar (around 460 nm), correspond exactly with the diffuse reflectance spectra. The ^1H n.m.r. spectra of the above series of nitroformazans show equivalent substituent groups on the phenyl rings with respect to the n.m.r. time scale (unchanged at -40 °C). Furthermore, if N(1) and N(5) are replaced by 96 atom-% ^{15}N in (1, Ar = Ph) the N*H* line at $\delta(CDCl_3)$ 15.28 becomes a triplet (1:2:1) with an apparent coupling constant of 45.5 Hz for both ^{15}N atoms (unchanged at -40 °C). This falls outside the normal range of ^{15}N-H coupling values (*ca.* 90 Hz for structurally related compounds)[16] and could indicate an averaging of the ^{15}N-H coupling over two chemically equivalent nitrogen sites consistent with a very rapid tautomeric equilibrium (as 1a $\rightleftharpoons$ 1b), but it does not exclude the mesomeric structure 2. This structure is certainly supported by the *X*-ray analysis reported here and even if, upon dissolution in chloroform, an extremely rapid tautomeric equilibrium does exist, the special kind of tautomerism involved in the case of the symmetrical closed-ring *syn*,s-*cis* formazans (which amounts simply to a movement of electrons and slight displacement of the imino proton, rather than an actual migration of a hydrogen atom such as occurs in keto-enol tautomeric systems like acetylacetone) must have an extremely small energy of activation. From this point of view, such an extremely rapid and facile proton exchange may (in the limit as the rate of exchange becomes very large) produce an effect equivalent to, and indistinguishable from, a single electron-delocalized mesomeric structure.

We thank the Council for Scientific and Industrial Research (Pretoria) for the diffractometer data collection and the C.S.I.R. and the University of Cape Town for research grants.

References and Notes

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2. J. Preuss and A. Gieren, *Acta Cryst.*, B31, 1276 (1975); A. T. Hutton, H. M. N. H. Irving, L. R. Nassimbeni, and G. Gafner, *Acta Cryst.*, B35, 1354 (1979).
3. Yu. A. Omel'chenko, Yu. D. Kondrashev, S. L. Ginzburg, and M. G. Neigauz, *Kristallografiya*, 19, 522 (1974) [*Sov. Phys. Cryst. (Engl. Transl.)*, 19, 323 (1974)]; M. Laing, *J. Chem. Soc. Perkin Trans. II*, 1248 (1977); J. Guillerez, C. Pascard, and T. Prangé, *J. Chem. Res. (S)*, 308; *(M)*, 3934 (1978); A. T. Hutton, H. M. N. H. Irving, and L. R. Nassimbeni, *Acta Cryst.*, B36, 2071 (1980).
4. D. Dale, *J. Chem. Soc. (A)*, 278 (1967); S. Balt, W. E. Renkema, C. van Capelleveen, and C. H. Stam, *J. Inorg. Nucl. Chem.*, 38, 459 (1976); W. E. Renkema, C. N. Lute, and C. H. Stam, *Acta Cryst.*, B35, 75 (1979).
5. F. A. Neugebauer, H. Fischer, and C. Krieger, *Chem. Ber.*, 112, 2369 (1979).
6. A. W. Nineham, *Chem. Rev.*, 55, 355 (1955).
7. a) C. Schiele, K. Halfar, and G. Arnold, *Tetrahedron*, 23, 2693 (1967); b) W. Otting and F. A. Neugebauer, *Z. Naturforsch.*, *Teil B*, 23, 1064 (1968); c) W. Otting and F. A. Neugebauer, *Chem. Ber.*, 102, 2520 (1969); d) G. Arnold and C. Schiele, *Spectrochim. Acta, Part A*, 25, 685 (1969).

8. a) G. V. D. Tiers, S. Plovan, and S. Searles, Jr., *J. Org. Chem.*, 25, 285 (1960); b) P. B. Fischer, B. L. Kaul, and H. Zollinger, *Helv. Chim. Acta*, 51, 1449 (1968); c) L. Mester, A. Stephen, and J. Parello, *Tetrahedron Lett.*, 4119 (1968).
9. Crystal data: $C_{17}H_{19}N_5O_2$, M_r = 325.4, monoclinic, space group $P2_1/n$, a = 16.419(8), b = 7.497(4), c = 13.443(6) Å, β = 90.69(5)°, V = 1654.6 Å^3, D_m = 1.29 (by flotation), Z = 4, D_c = 1.31 g cm^{-3}, $F(000)$ = 688. The structure was solved by direct methods using the SHELX-76 program system (G. M. Sheldrick, Cambridge) from data collected by the $\omega - 2\theta$ scan technique in the range $3 \leqslant \theta \leqslant 23°$ on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation [λ = 0.7107 Å, μ(Mo-K_α) = 0.53 cm^{-1}]. Refinement by full-matrix least-squares gave R = 0.063 for 1143 observed reflections with $I_{rel} > 2\sigma(I_{rel})$. The atomic co-ordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.
10. Selected bond lengths (Å; atom numbering follows from formula 1): N(1)-N(2) 1.298(5), N(4)-N(5) 1.301(5), C(3)-N(2) 1.346(6), C(3)-N(4) 1.322(6), N(1)-C(1) 1.421(6), N(5)-C(5) 1.436(6), C(3)-N(3) 1.484(6), N(3)-O(1) 1.234(5), and N(3)-O(2) 1.226(5). The non-bonded distance N(1)•••N(5) is 2.72(1) Å. Selected bond angles (°): C(1)-N(1)-N(2) 116.0(5), N(1)-N(2)-C(3) 117.0(5), N(2)-C(3)-N(4) 136.5(5), C(3)-N(4)-N(5) 117.2(5), and N(4)-N(5)-C(5) 116.7(5). Bond lengths show that the aryl groups are not conjugated with the formazan ring system; they are twisted out of its plane in similar senses, the ring attached to N(1) by 26°, that to N(5) by 36°. Electron delocalization does not extend to the nitro group which is 23° out of the formazan ring plane.
11. The bond orders used here correspond to 1 + P, where P is the double-bond character [L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, New York, pp. 232 - 240 (1960); H. J. Bernstein, *Trans. Faraday Soc.*, 57, 1649 (1961)], and were read off the curves given by M. Burke-Laing and M. Laing, *Acta Cryst.*, B32, 3216 (1976).
12. W. C. Hamilton, *Acta Cryst.*, 18, 502 (1965).
13. J.-O. Lundgren and I. Olovsson, in The Hydrogen Bond - Recent Developments in Theory and Experiments, Vol. II, edited by P. Schuster, G. Zundel and C. Sandorfy, North-Holland Publishing Company, Amsterdam, pp. 503, 505 (1976).
14. The lack of observed ν(N-H) in *syn*,s-*cis* formazans has been noted previously, *e.g.*, ref. 7b. A temperature sensitive band at *ca.* 3030 cm^{-1} has been assigned to ν(N-H) in these compounds but we have found that this weak band does not move on deuteration (ref. 7d).
15. J. B. Gill, H. M. N. H. Irving, and A. Prescott, *J. Chem. Soc. Perkin Trans. II*, 1683 (1977).
16. T. Axenrod, in Nitrogen NMR, edited by M.Witanowski and G. A. Webb, Plenum Press, London, pp. 261 - 317 (1973). See also ref. 8c. In contrast, we have found that 3-chloro-1,5-diphenylformazan, which is a yellow solid with a $\lambda_{max.}$ in chloroform at 410 nm and is probably in the open chain *anti*,s-*trans* configuration, gave an ^{15}N*H* resonance at δ($CDCl_3$) 8.72 [doublet, $^1J(^{15}N\text{-}H)$ = 91.1 Hz] and an obvious ν(N-H) at 3258 cm^{-1} in CCl_4.

(Received in UK 21 July 1981)