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The Structure of 1,5-Bis(2,6-dimethylphenyl)-3-nitroformazan

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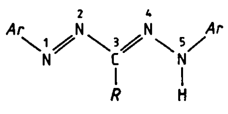
Abstract

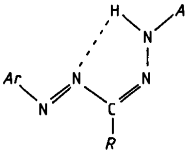
$C_{17}H_{19}N_5O_2$ is monoclinic, space group $P2_1/n$, with $a = 16{\cdot}419$ (8), $b = 7{\cdot}497$ (4), $c = 13{\cdot}443$ (6) Å, $\beta = 90{\cdot}69$ (5)°, $Z = 4$. The structure was refined to $R = 0{\cdot}063$ for 1143 observed reflections. The N—N—C—N—N chain adopts the closed-ring *syn,s-cis* configuration relative to the formal double C=N and single C—N bonds; electron delocalization within this planar ring results in a structure best described as mesomeric.

Introduction

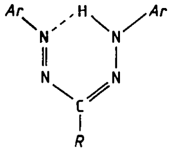
X-ray crystallographic investigations of formazans have yielded examples of both the *anti,s-trans* (1) and *syn,s-trans* (2) configurations relative to the formal double C=N and single C—N bonds (Table 1), but until recently no instance of the closed-ring *syn,s-cis* isomer (3) had been reported, although this configuration is adopted when 3-methyl-1(or 5)-phenyl-5(or 1)-*p*-tolylformazan deprotonates to form the bis-chelate with Ni^{II} by coordination through N(1) and N(5) (Dale, 1967), when 1-(2-hydroxyphenyl)-3,5-diphenylformazan acts as a terdentate ligand to complex with Cu^{II} or Ni^{II} through N(1), N(5), and O (the fourth coordination site being satisfied by NH_3) (Renkema, Lute & Stam, 1979), and when 1,5-diphenylformazan coordinates through N(1) and N(4) as a non-ionized ligand to form a bis-chelated Cu^{I} cation (Balt, Renkema, van Capelleveen & Stam, 1976).



(1) *anti,s-trans*



(2) *syn,s-trans*



(3) *syn,s-cis*

Table 1. *Configurations of formazans confirmed by X-ray analysis*

anti,s-trans

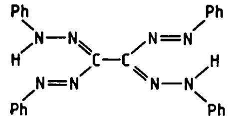
1,5-Diphenylformazan [(1); Ar = Ph, R = H] (*a*)
1,5-Diphenyl-3-thioformazan ('dithizone') [(1); Ar = Ph, R = SH] (*b*)
3-Isopropylthio-1,5-diphenylformazan [(1); Ar = Ph, $R = SCH(CH_3)_2$] (*c*)
3-Methylthio-1,5-di(*o*-tolyl)formazan [(1); Ar = *o*-tolyl, $R = SCH_3$] (*d*)

syn,s-trans

3-Methylthio-1,5-diphenylformazan [(2); Ar = Ph, $R = SCH_3$] (*e*)
3-Carboxymethylthio-1,5-diphenylformazan [(2); Ar = Ph, $R = SCH_2CO_2H$] (*f*)

References: (*a*) Omel'chenko, Kondrashev, Ginzburg & Neigauz (1974). (*b*) Laing (1977). (*c*) Guillerez, Pascard & Prangé (1978). (*d*) Hutton, Irving & Nassimbeni (1980). (*e*) Preuss & Gieren (1975). (*f*) Hutton, Irving, Nassimbeni & Gafner (1979).

Recently, however, the structure of 'diformazyl', which had been formulated as 1,1′,5,5′-tetraphenyl-3,3′-biformazan (4), was shown to be 5-[bis(phenylazo)methylene]-1,3-diphenyltetrazoline betaine [(5) and canonical forms] by X-ray structure analysis of the hydrochloride and by degradation reactions of the base (Neugebauer, Fischer & Krieger, 1979). The hydrochloride adopts a closed-ring *syn,s-cis* structure (6) and provides the first crystallographic evidence for this configuration in an uncoordinated formazan. Confirmation of the postulated *syn,s-cis* structure for the series of red formazans in general was sought in the present study of the title compound [(3); Ar = 2,6-dimethylphenyl, $R = NO_2$] (Nineham, 1955; Hooper, 1969; Hutton, 1980).



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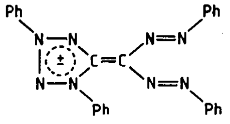

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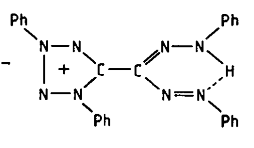

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Experimental

Preparation

The compound was prepared by coupling the diazonium cation of 2,6-dimethylaniline with nitromethane in 2:1 molar proportion. The small amount of red oily product (~1% yield) was extracted into chloroform and purified by chromatography (alumina/benzene). The yield from the diazonium coupling reaction could not be improved even upon varying the conditions widely (Hutton, 1980). Recrystallization from ethanol gave dark-red needles elongated along **b** with m.p. 390–393 K. (Composition: found: C 62·55, H 5·9, N 21·3%; calculated for $C_{17}H_{19}N_5O_2$: C 62·8, H 5·85, N 21·5%.)

Additional crystal and intensity data

$C_{17}H_{19}N_5O_2$, M_r = 325·4, V = 1654·6 Å^3, D_m = 1·29 (by flotation in aqueous KI), D_c = 1·31 Mg m^{-3}, $F(000)$ = 688; Mo $K\alpha$ radiation, λ = 0·7107 Å; μ(Mo $K\alpha$) = 0·053 mm^{-1}. Systematic absences $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$.

Preliminary cell dimensions and space-group symmetry were determined from photographs. A single crystal 0·4 × 0·2 × 0·2 mm was used for data collection. Accurate cell dimensions were obtained by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Intensities were collected by the ω–2θ scan technique [scan width 1·2° (θ), scan speed 0·03° (θ) s^{-1}] in the range $3 \leq \theta \leq 23°$. The intensities of three reference reflections monitored after every 68 measured reflections remained constant to within ±1·3% of their mean values. 2506 reflections were collected, of which 1143 unique reflections [$I > 2\sigma(I)$] were employed in the analysis. Lorentz–polarization corrections were applied but no correction was made for absorption.

Solution and refinement of the structure

The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1978). Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) for C, N and O, and from Stewart, Davidson & Simpson (1965) for H, with anomalous-dispersion corrections from Cromer & Liberman (1970). The final full-matrix least-squares refinement was carried out with all the heavy atoms treated anisotropically. The aromatic and methyl H atoms, most of which had been revealed in previous difference Fourier maps, were constrained to ride at 1·08 Å from their corresponding parent C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as two single parameters, the methyl H atoms being refined as rigid groups.

Up to this point of the refinement (R = 0·070) the imino H atom had been omitted from the model. A difference Fourier synthesis was then computed using all atoms except the imino H in the calculation. This H atom was located (Fig. 1) midway between N(1) and N(5) completing a hexagonal formazan ring. It was also observed at this stage that the two N—N distances were virtually identical and midway between single- and double-bond lengths. The imino H atom 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. The N···H distance refined to 1·50 (3) Å. The refinement converged at R = 0·059 and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$ = 0·045 with $w = 1/(\sigma^2 F_o)$. It was considered possible, however, that the single peak found for the imino H atom (Fig. 1) could have resulted from the sum of two smaller peaks derived from half H atoms on each terminal N atom. The final refinement was therefore repeated and the single H atom previously constrained to be equidistant from N(1) and N(5) was replaced by two half H atoms [H(N1) and H(N5)] each fixed at 1·08 Å from the parent N atom in sp^2 geometry. The site-occupancy factors (s.o.f.'s) of H(N1) and H(N5) were refined so that their sum was always unity. After the same number of full-matrix least-squares refinements as were used in the initial model the isotropic temperature factor for 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 and R_w to 0·048 using the same weighting function as in the initial model. U(aromatic H) was 0·102 (9) and U(methyl H) 0·125 (7) Å^2. In the final cycle the mean e.s.d. in the parameters of the non-hydrogen atoms was >100 times the average

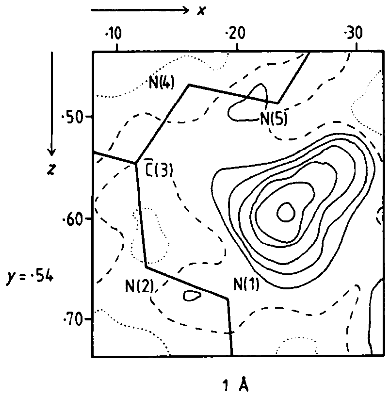

Fig. 1. Difference electron density map in the region of the N atoms after refinement with the imino H omitted from the model. Contours are at intervals of 0·02 e Å^{-3}; negative contours are dotted, the zero line is broken.

parameter shift. A final difference map showed no peaks >0·06 e Å^{-3}. Besides providing a physically reasonable N—H distance, this model results in a significantly lower temperature factor for the (probably disordered) imino proton, while the slight increase in the residual indices is insignificant (Hamilton, 1965; Hutton, 1980). This model was therefore chosen to be reported in full.* The final 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 & Olovsson (1976) have pointed out that it is practically impossible to differentiate, on the basis of diffraction data alone, between two overlapping disordered H peaks and a truly single central peak. Table 2 lists the final positions of the non-hydrogen atoms and their equivalent isotropic thermal parameters.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *of the non-hydrogen atoms and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

	x	y	z	U_{eq}*
N(1)	1922 (3)	6102 (5)	6860 (3)	50 (5)
N(2)	1241 (3)	6731 (6)	6507 (3)	49 (5)
N(3)	334 (3)	7443 (7)	5219 (4)	65 (7)
N(4)	1586 (3)	6269 (6)	4736 (3)	53 (5)
N(5)	2314 (3)	5653 (6)	4916 (4)	52 (6)
O(1)	64 (2)	6995 (6)	4396 (3)	89 (6)
O(2)	−22 (3)	8411 (6)	5807 (3)	87 (6)
C(3)	1149 (3)	6751 (7)	5511 (5)	48 (7)
C(11)	1996 (4)	6042 (7)	7914 (4)	52 (7)
C(12)	1318 (4)	5932 (7)	8546 (4)	62 (8)
C(13)	1471 (5)	5928 (8)	9564 (5)	81 (9)
C(14)	2250 (5)	5984 (8)	9943 (5)	82 (10)
C(15)	2913 (4)	6037 (8)	9321 (5)	72 (9)
C(16)	2797 (4)	6042 (7)	8296 (4)	55 (7)
C(17)	445 (3)	5706 (8)	8185 (4)	84 (9)
C(18)	3520 (3)	6135 (8)	7631 (4)	69 (8)
C(51)	2781 (4)	5119 (7)	4070 (4)	49 (7)
C(52)	2412 (4)	4368 (7)	3224 (4)	57 (7)
C(53)	2939 (4)	3850 (8)	2458 (5)	70 (8)
C(54)	3768 (4)	4089 (9)	2519 (5)	79 (9)
C(55)	4108 (4)	4832 (8)	3365 (5)	67 (8)
C(56)	3619 (4)	5373 (7)	4155 (4)	55 (7)
C(57)	1523 (3)	3981 (7)	3106 (4)	83 (9)
C(58)	3998 (3)	6192 (8)	5067 (4)	75 (8)

* $U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with *SHELX* 76 (data reduction, structure solution and refinement), *XANADU* (molecular geometry) and *PLUTO* (illustrations) (Sheldrick, 1978; Roberts & Sheldrick, 1975; Motherwell, 1975).

Description of the structure

The molecular structure and atomic nomenclature are shown in Fig. 2, while Table 3 lists bond lengths and angles. The title formazan crystallizes in the closed

Table 3. *Bond lengths* (Å) *and angles* (°)

C(11)–C(12)	1·411 (6)	N(3)–O(2)	1·226 (5)
C(12)–C(13)	1·388 (7)	C(3)–N(4)	1·322 (6)
C(13)–C(14)	1·372 (8)	N(4)–N(5)	1·301 (5)
C(14)–C(15)	1·381 (7)	N(5)–C(51)	1·436 (6)
C(15)–C(16)	1·389 (6)	C(51)–C(52)	1·400 (6)
C(16)–C(11)	1·406 (7)	C(52)–C(53)	1·408 (7)
C(12)–C(17)	1·517 (6)	C(53)–C(54)	1·374 (7)
C(16)–C(18)	1·496 (7)	C(54)–C(55)	1·378 (7)
C(11)–N(1)	1·421 (6)	C(55)–C(56)	1·399 (7)
N(1)–N(2)	1·298 (5)	C(56)–C(51)	1·392 (7)
N(2)–C(3)	1·346 (6)	C(52)–C(57)	1·495 (6)
C(3)–N(3)	1·484 (6)	C(56)–C(58)	1·500 (6)
N(3)–O(1)	1·234 (5)		

C(11)–C(12)–C(13)	117·3 (6)	C(3)–N(3)–O(1)	117·1 (6)
C(12)–C(13)–C(14)	121·5 (7)	C(3)–N(3)–O(2)	118·2 (5)
C(13)–C(14)–C(15)	120·9 (7)	O(1)–N(3)–O(2)	124·8 (6)
C(14)–C(15)–C(16)	120·1 (6)	C(3)–N(4)–N(5)	117·2 (5)
C(15)–C(16)–C(11)	118·6 (6)	N(4)–N(5)–C(51)	116·7 (5)
C(16)–C(11)–C(12)	121·4 (5)	N(5)–C(51)–C(56)	115·7 (5)
C(11)–C(12)–C(17)	124·3 (5)	N(5)–C(51)–C(52)	121·7 (5)
C(13)–C(12)–C(17)	118·3 (6)	C(51)–C(52)–C(53)	116·2 (6)
C(11)–C(16)–C(18)	121·8 (5)	C(52)–C(53)–C(54)	122·5 (6)
C(15)–C(16)–C(18)	119·5 (6)	C(53)–C(54)–C(55)	119·5 (6)
C(12)–C(11)–N(1)	122·9 (5)	C(54)–C(55)–C(56)	120·9 (6)
C(16)–C(11)–N(1)	115·6 (5)	C(55)–C(56)–C(51)	118·3 (6)
C(11)–N(1)–N(2)	116·0 (5)	C(56)–C(51)–C(52)	122·6 (6)
N(1)–N(2)–C(3)	117·0 (5)	C(51)–C(52)–C(57)	125·2 (6)
N(2)–C(3)–N(4)	136·5 (5)	C(53)–C(52)–C(57)	118·5 (6)
N(2)–C(3)–N(3)	110·9 (5)	C(51)–C(56)–C(58)	121·5 (5)
N(4)–C(3)–N(3)	112·5 (5)	C(55)–C(56)–C(58)	120·2 (6)

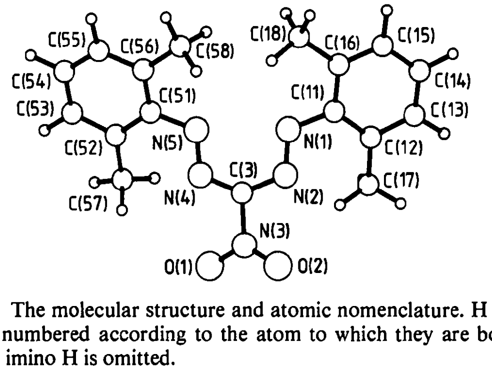

Fig. 2. The molecular structure and atomic nomenclature. H atoms are numbered according to the atom to which they are bonded. The imino H is omitted.

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* The analysis of variance, lists of structure factors, H-atom coordinates, anisotropic thermal parameters, torsion angles and least-squares-planes parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36352 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

syn,s-cis configuration [as (3)] with the imino proton forming an intramolecular hydrogen bridge [N(1)···N(5) 2·72 (1) Å] to give a six-membered 'formazan ring'. The bond lengths reveal extensive delocalization of π electrons within the N—N—C—N—N chain. The two N—N distances are virtually identical, with bond orders of 1·58 [read off Burke-Laing & Laing's (1976) standard curves], while the two C—N distances within the formazan ring show bond orders of 1·47 [C(3)—N(2)] and 1·62 [C(3)—N(4)]. The expected planarity of the N—N—C—N—N chain consequent on electron delocalization is confirmed by the torsion angles in the chain which are close to 0°. A list of torsion angles has been deposited, as well as parameters for several least-squares planes (see deposition footnote). The largest deviation of an atom in the chain from the N—N—C—N—N plane is 0·02 Å; Fig. 3 illustrates this planarity and also shows that the aryl and nitro groups are somewhat twisted out of this plane. Consideration of (Ar)C—N bond lengths shows that the aryl groups are essentially not conjugated with the formazan ring system (bond orders *ca* 1·1); they are twisted out of its plane in similar senses, ring (1) by 26° and ring (5) by 36° (Fig. 3). In related compounds, *e.g.*, 3-methylthio-1,5-di(*o*-tolyl)formazan [(1); Ar = *o*-tolyl, $R = SCH_3$], the delocalization in the N—N—C—N—N chain extends to the aryl groups to a much larger degree (Hutton, Irving & Nassimbeni, 1980). The presence of methyl groups in the 2- and 6-positions on both aryl rings clearly results in the rings being twisted out of the N—N—C—N—N plane, resulting in diminished *p*-orbital interaction and a consequent decrease in π-electron delocalization. Relevant non-bonded distances are given in Table 4.

The nitro-group plane forms an angle of 23° with the formazan-ring plane, thereby decreasing non-bonded interactions between the lone-pair orbitals on N and O atoms (Table 4). The formazan-chain–nitro linkage C(3)—N(3) [1·484 (6) Å] compares with 1·475 (10) Å in nitromethane (*International Tables for X-ray Crystallography*, 1968) and is a single bond: electron delocalization in the formazan ring does not extend to the nitro group. However, the electron-withdrawing nitro group polarizes the σ-electron density along the C(3)—N(3) bond, thus reducing the repulsion between the σ electrons of this bond and those of the C(3)—N(2) and C(3)—N(4) bonds, allowing the N(2)—C(3)—N(4) bond angle to open from the expected sp^2 angle of 120 to 136°. The N—O bond lengths are nearly equivalent and are normal for nitro compounds. Bond distances and angles relating to the aryl groups are satisfactory; the mean aromatic C—C distance in the two rings is 1·392 (13) Å, while the mean C—CH_3 distance is 1·502 (10) Å.

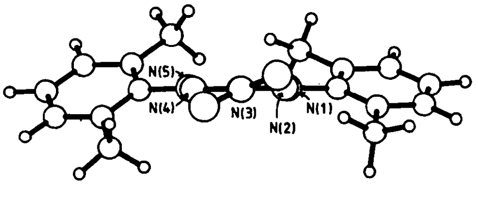


Fig. 3. View down the N(3)—C(3) bond showing the planarity of the formazan ring and the twisting of the aryl and nitro groups out of this plane.

Table 4. *Selected intramolecular non-bonded distances* (Å)

N(1)···N(5)	2·72 (1)	N(5)···C(58)	2·80 (1)
N(1)···C(18)	2·81 (1)	N(2)···O(2)	2·59 (1)
N(2)···C(17)	2·73 (1)	N(4)···O(1)	2·59 (1)
N(4)···C(57)	2·78 (1)		

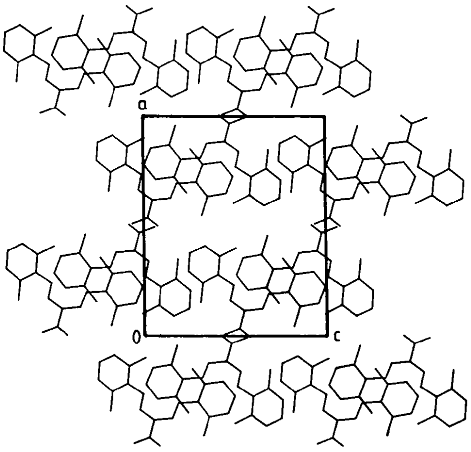
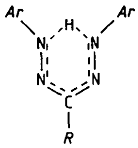


Fig. 4. View of the molecular packing along **b**. H atoms are omitted.

A projection of the molecular packing along **b** is shown in Fig. 4; molecules are stacked in alternate directions along **b**. No intermolecular separations less than the sum of the van der Waals radii (Bondi, 1964) occur.

Conclusion

In the structure of the hydrochloride of 'diformazyl' (6) (Neugebauer, Fischer & Krieger, 1979) the imino H atom was found on N(1) and N(5) with s.o.f.'s of 0·35 and 0·65, respectively, and the formal single and double bonds in the N—N—C—N—N chain were clearly distinguishable and corresponded to the fraction of H atom on each of the terminal N atoms. The present structure, however, shows a half H atom associated with each terminal N atom and apparent equivalence of chemical bonds, which would be distinct in individual tautomers. The co-existence of two distinct 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 (3) (Ar = 2,6-dimethylphenyl, R = NO_2) and the equivalent form 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 (7) (Ar = 2,6-dimethylphenyl, R = NO_2). In molecular-orbital parlance the system would simply be described as 'electron-delocalized'. In this description the precise location of the imino H atom 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, which itself may be nearly symmetrical.



(7)

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