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AZO–HYDRAZONE TAUTOMERISM IN AZO DYES. III. THE TAUTOMERIC STRUCTURE OF 1-(4'-NITROPHENYLAZO)-2-NAPHTHYLAMINE FROM CRYSTAL STRUCTURE DETERMINATION[1]

J. KELEMEN,†[a] G. KORMÁNY[a] and G. RIHS[b]

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[a] *Research and Development Department, Dyestuff and Chemicals Division*

and

[b] *Central Function Research, Physics Department, Ciba–Geigy Ltd, Basle, Switzerland*

SUMMARY

The structure of **1**(NO_2)*–dioxane 2:1 solvate single crystal has been determined by direct methods and refined by analysis of the three-dimensional Mo K*α *intensity data. The unit cell is monoclinic, space group* $P2_1/c$ *with* $a = 8{\cdot}960(3)$, $b = 6{\cdot}386(2)$, $c = 30{\cdot}141(11)$ Å, $\beta = 108{\cdot}56(2)°$. *Least-squares refinement of all positional and thermal parameters (hydrogen atoms isotropic) with 1458 independent reflections out of 2817 gave a final R-index of 0·069. The dye molecule is almost planar and of* trans *configuration. The nitro group, however, is significantly twisted out of the molecular best plane. Six-membered chelate ring structures are formed by intramolecular* N—H···N *bonds while intermolecular* N—H···O *interactions give rise to complex formation involving two dye and one dioxane molecules in a centrosymmetrical arrangement. Two such complexes are accommodated in the unit cell.*

Based on the observed molecular geometry and quantum chemical (SCF–MO) calculation of bond dimensions a strong predominance of the azo tautomer was concluded for **1**(NO_2). *This assignment is further supported by empirical correlations, using CN and NN bond distances from a great variety of reported azo and hydrazone structures which are compiled here for the first time. The mobile hydrogen is attached to the amine nitrogen* [$R(NH) = 1{\cdot}04(5)$ Å] *thereby excluding a major participation of the hydrazone form. These findings compare well with those for solutions*[1] *and are in accordance with previous quantum chemical predictions.*[2]

† Author to whom correspondence should be addressed.

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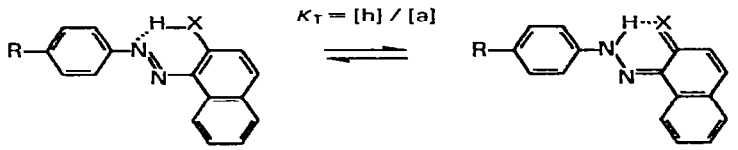
1. INTRODUCTION

Previous papers of this series[1,2] have dealt with the tautomeric equilibria of 1-phenylazo-2-naphthylamine (**1**) and 1-phenylazo-2-naphthol (**2**) dyes in solution without reference to their solid structure. X-ray investigation of dyes in the crystalline state has, however, direct practical relevance, since in pigment application the colourants are used in the form of discrete crystalline particles; not only size,[3] shape [4] and crystallographic arrangement[5] affect their colourant properties but to a great extent also the position of the tautomeric equilibria within the crystalline framework.



a h

1 (R) : X = NH, R = H, NO_2
2 (R) : X = O, R = H, NO_2

From IR measurements the presence of both tautomers in the same crystal, termed the 'mixed tautomeric crystal lattice',[6] has been concluded for 1-phenylazo-2-naphthol,[7] 2-phenylazo-[7] and 4-phenylazo-1-naphthol[8] and for some nitro, and dinitrophenylazo-alkylphenols.[6] For these, solvent-dependent mobile equilibria were established in solution,[9,10] suggesting that the free energy of the tautomers is of comparable magnitude. In such cases crystal structure analysis was predicted to yield intermediate bond dimensions.[7] Indeed, examples confirming this prediction have been later found for 1-(2-thiazolylazo)-2-naphthol and its 6-bromo derivative (cf. section 4).

Another observation concerns 4-phenylazo-1-naphthol, which crystallizes in the azo form from pyridine and in the hydrazone form from acetic acid, as determined by X-ray diffraction analysis and IR spectra.[11] The non-chelated terminal oxygen functions (OH and C=O respectively) are more susceptible toward H-bonding with solvent molecules than are the azo or NH groups, thus leading to a greater stabilization of the azo form in pyridine and to a preference for the hydrazone in AcOH solution.[9d] Similar behaviour is conceivable in a crystal built from solvated dye complex units. Unfortunately, from the paper quoted[11] it was not apparent whether or not the solvent was incorporated in the lattice.

For the naphthylamines, **1** (R = MeO, CN, NO_2), a strong azo preference of the equilibrium has been found in various solvents by UV, Raman and NMR measurements,[1,2] in agreement with the greater stability of the azo tautomer derived from quantum chemical calculations.[2]

On these grounds, it was therefore expected that no mixed, tautomeric crystal lattice will be encountered with 1-phenylazo-2-naphthylamines and X-ray investigation should afford sensible results. Furthermore, the prototropic hydrogen is confined to a stable six-membered chelate ring[12] and therefore, the influence on the equilibrium position of intermolecular hydrogen bonds was thought to be negligible.

In order to prove the azo predominance in the solid state of the naphthylamine series (**1**), it will suffice to show that the equilibrium is shifted far to the azo side also in the crystal of **1**(NO_2). Based on HMO arguments a progressive hydrazonic shift is expected in both series (**1** and **2**) with increasing electron acceptor strength of the substituent R.[2,13] Indeed, NMR studies indicated that K_T of **2** runs parallel to the Hammett σ-value of R.[10] It is therefore realistic to assume that weaker acceptor substituents (e.g. CN) or electron donors (e.g. MeO) will stabilize the azo structure relative to the hydrazone even more than in **1**(NO_2).

We report now on the crystal structure of **1**(NO_2) single crystal, grown from dioxane by slow evaporation of the solvent at room temperature. Both microanalysis and X-ray data revealed the inclusion of solvent in a 2:1 dye to dioxane ratio. The crystal structure of the closely related **2**(NO_2) was reported by Grainger and McConnell.[14] Their data are utilized for comparison and as a check for the validity of the theoretical calculations performed to aid tautomer assignment. The hydrazone form is the preferred tautomer of this dye in solution.[9a]

The numbering scheme used for both dyes in this work is shown in Fig. 1.

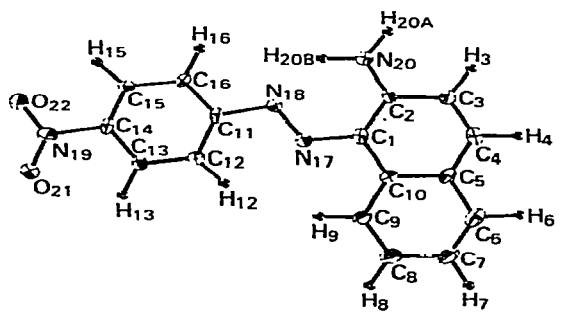


Fig. 1. An ORTEP plot with numbering scheme for **1**(NO_2). The thermal ellipsoids are drawn at 20% probability. In the numbering of **2**(NO_2), O_{20} replaces N_{20}. No hydrogen atom positions were given for the latter.[14]

2. EXPERIMENTAL

1(NO_2) was prepared by coupling diazotized *p*-nitroaniline on 2-naphthylamine-1-sulphonate sodium salt[15] and recrystallized from chlorobenzene–hexane (1:1) until chromatographic purity (by tlc) was attained. M.p. 186–7 °C (lit.[16] 185–7 °C). Calculated for $C_{16}H_{12}N_4O_2$ (%): C, 65·75; H, 4·14; N, 19·17; O, 10·95. Found (%): C, 65·93; H, 4·00; N, 19·00.

Specimen from dioxane: m.p. 180–1 °C. Calculated for $C_{16}H_{12}N_4O_2.1/2(C_4H_8O_2)$ (%): C, 64·28; H, 4·79; N, 16·66; O, 14·27. Found (%): C, 64·03; H, 4·75; N, 16·73.

2.1. Crystal structure analysis

Studies were carried out on a crystal of dimensions (mm) 0·5 × 0·4 × 0·1 obtained from dioxane solution. Cell dimensions (Table 1) were determined by a least-squares fit to the settings of 12 high-order reflections (Mo$K\alpha_1$, $\lambda = 0{\cdot}70926$ Å). Intensity data were collected on a Picker-FACS-I diffractometer (Mo$K\alpha$, graphite monochromator): 2817 independent reflections in the range $2\Theta = 2$–$48°$ were measured using Θ–2Θ scan mode. The intensities of three standard reflections, measured at intervals of 50 reflections, did not show any evidence of crystal decay throughout the data collection. Lorentz and polarization corrections were applied but none was made for absorption.

TABLE 1
CELL DATA OF **1**(NO_2)–DIOXANE 2:1 SOLVATE

Composition	$C_{16}H_{12}N_4O_2.1/2C_4H_8O_2$
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	8·960(3)
b(Å)	6·386(2)
c(Å)	30·141(11)
β(°)	108·56(2)
M	336·4
V(Å^3)	1635
Z	4
Number of reflections included in least-squares refinement	1458

The structure was solved by direct methods with the computer program MULTAN 77.[17] All non-hydrogen atoms could be located in an *E*-map corresponding to the highest figure of merit. The *R*-index converged after refinement of the positional and thermal (first isotropic and then anisotropic) parameters in a block diagonal least-squares procedure to 0·092. The hydrogen atom positions were obtained from a difference map. Inclusion of the positional and isotropic thermal hydrogen atom parameters in the least-squares refinement lowered the *R*-index to 0·069. The final atomic parameters are given in Table 2.

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES OF I(NO_2)–DIOXANE 2:1 SOLVATE[a]

	X	Y	Z
Dye molecule			
C(1)	0·9689(6)	0·0516(9)	0·8407(2)
C(2)	1·1151(6)	0·1405(8)	0·8660(2)
C(3)	1·1610(6)	0·3311(9)	0·8492(2)
C(4)	1·0639(7)	0·4272(9)	0·8108(2)
C(5)	0·9163(6)	0·3436(9)	0·7849(2)
C(6)	0·8124(7)	0·4422(9)	0·7443(2)
C(7)	0·6736(7)	0·3599(9)	0·7203(2)
C(8)	0·6269(7)	0·1678(9)	0·7344(2)
C(9)	0·7210(6)	0·0667(9)	0·7731(2)
C(10)	0·8669(6)	0·1499(9)	0·7995(2)
C(11)	0·9077(6)	−0·4117(8)	0·8984(2)
C(12)	0·7611(6)	−0·4737(9)	0·8692(2)
C(13)	0·6976(6)	−0·6588(9)	0·8801(2)
C(14)	0·7838(6)	−0·7684(9)	0·9195(2)
C(15)	0·9260(6)	−0·7080(9)	0·9483(2)
C(16)	0·9904(6)	−0·5241(9)	0·9380(2)
N(17)	0·9072(5)	−0·1296(7)	0·8535(1)
N(18)	0·9861(5)	−0·2273(7)	0·8906(1)
N(19)	0·7076(5)	−0·9645(7)	0·9286(2)
N(20)	1·2134(5)	0·0573(7)	0·9056(2)
O(21)	0·5863(4)	−1·0256(7)	0·9013(1)
O(22)	0·7769(5)	−1·0507(7)	0·9666(1)
H(3)	1·274(5)	0·404(7)	0·868(2)
H(4)	1·093(5)	0·575(8)	0·801(2)
H(6)	0·847(5)	0·598(8)	0·737(2)
H(7)	0·601(5)	0·428(8)	0·690(2)
H(8)	0·518(5)	0·101(8)	0·717(2)
H(9)	0·689(5)	−0·077(8)	0·785(2)
H(12)	0·705(5)	−0·384(8)	0·839(2)
H(13)	0·583(5)	−0·713(8)	0·857(2)
H(15)	0·973(5)	−0·806(8)	0·977(2)
H(16)	1·102(5)	−0·476(8)	0·959(2)
H(20A)	1·314(5)	0·130(8)	0·921(2)
H(20B)	1·178(5)	−0·083(8)	0·917(2)
Dioxane molecule			
O(23)	0·5269(5)	0·6528(6)	0·0346(1)
C(24)	0·4825(7)	0·4417(9)	0·0427(2)
C(25)	0·5378(7)	0·2924(9)	0·0136(2)
H(24A)	0·544(5)	0·412(8)	0·081(2)
H(24B)	0·344(5)	0·441(8)	0·035(2)
H(25A)	0·510(6)	0·143(7)	0·020(2)
H(25B)	0·657(5)	0·300(8)	0·024(2)

[a] Estimated standard deviations of the last digit are given in parentheses. Hydrogen atoms are given the number of the heavy atom to which they are attached.

3. TAUTOMERIC EQUILIBRIUM POSITION ASSESSED BY SCF–MO CALCULATIONS

Azo and hydrazone tautomers are expected to differ markedly in the bond lengths along the C_{11}–N_{18}–N_{17}–C_1–C_2–X_{20} path. In order to find the prevalent tautomer, bond dimensions, in particular those which define this region, will be compared here with interatomic separations obtained from a quantum chemical procedure, and in the next section empirical correlations will be considered.

For the theoretical calculations the π-electron SCF–LCAO–MO theory of Pople[18] was adopted taking advantage of the parameterization scheme developed by Dewar and co-workers.[19,20] This method has been proved to reproduce experimental bond lengths very closely.[20,21] Actually, method and parameters used

TABLE 3

BOND LENGTHS INVOLVING NON-HYDROGEN ATOMS OF **1(NO$_2$)** FROM CRYSTAL STRUCTURE DETERMINATION[a] AND THOSE OF THE PARENT **1(H)** TAUTOMERIC PAIR FROM SCF–MO CALCULATIONS

Bond	**1(NO$_2$)**	**1(H)–a**	**1(H)–b**
Azo group			
C(1)–N(17)	1·388(7)[b]	1·384(−4)[c]	1·301(−87)[c]
N(17)–N(18)	1·279(6)	1·260(−19)	1·361(+82)
N(18)–C(11)	1·428(7)	1·400(−28)	1·380(−48)
Naphthalene group			
C(2)–N(20)	1·348(7)	1·371(+23)	1·294(−54)
C(1)–C(2)	1·408(8)	1·393(−15)	1·464(+56)
C(2)–C(3)	1·429(8)	1·432(+3)	1·463(+34)
C(3)–C(4)	1·353(8)	1·370(+17)	1·352(−1)
C(4)–C(5)	1·409(8)	1·432(+23)	1·461(+52)
C(5)–C(6)	1·427(8)	1·424(−3)	1·402(−25)
C(6)–C(7)	1·331(9)	1·376(+45)	1·393(+62)
C(7)–C(8)	1·405(9)	1·420(+15)	1·400(−5)
C(8)–C(9)	1·364(9)	1·376(+12)	1·393(+29)
C(9)–C(10)	1·401(8)	1·424(+23)	1·403(+2)
C(10)–C(1)	1·432(8)	1·434(+2)	1·461(+29)
C(10)–C(5)	1·429(8)	1·403(−26)	1·404(−25)
Benzene group			
C(11)–C(12)	1·386(8)	1·400(+14)	1·405(+19)
C(12)–C(13)	1·395(8)	1·396(+1)	1·394(−1)
C(13)–C(14)	1·383(8)	1·396(+13)	1·397(+14)
C(14)–C(15)	1·350(8)	1·398(+48)	1·397(+47)
C(15)–C(16)	1·386(8)	1·394(+8)	1·394(+8)
C(16)–C(11)	1·388(8)	1·402(+14)	1·405(+17)
Nitro group			
C(14)–N(19)	1·493(7)		
N(19)–O(21)	1·200(6)		
N(19)–O(22)	1·243(6)		

[a] In the **1(NO$_2$)**–dioxane 2:1 solvate, bond length of dioxane: C–C 1·483(8), C–O 1·448(7) and 1·426(7) Å.

[b,c] Estimated standard deviations ([b]) and differences between calculated and determined bond lengths ([c]) in the last significant figures are given in parentheses.

were those of Dewar and Morita[20] but polarization of the σ-core was neglected. The bond lengths have been recalculated in every iterative cycle ('variable β' approach[19,20]). The nitro group could not be included in the calculation for lack of thermochemical data necessary for the evaluation of the N—O resonance integral.

Table 3 and Fig. 2a compare the bond lengths of **1(NO$_2$)** from our X-ray work with those calculated for the azo (**a**) and hydrazone (**h**) tautomers of the parent dye **1(H)**. In the $C_{11}\cdots N_{20}$ region of **1(NO$_2$)**, listed as the first five entries in Table 3, the experimental bond lengths correlate well with the calculated **1(H)–a** bond distances (correlation coefficient $r = 0{\cdot}944$) whereas the agreement with the **1(H)–h** bond lengths is poor ($r = 0{\cdot}333$). Except for two bonds, experimental distances differ along the entire molecule by less than 0·03 Å from those calculated for the azo tautomer. The two deviating bonds, C_6—C_7 and C_{14}—C_{15}, measure 1·339 and 1·350 Å by X-ray diffraction and appear to be anomalously short. The corresponding theoretical values (1·376 and 1·398 Å) are more reasonable for aromatic C—C bonds.

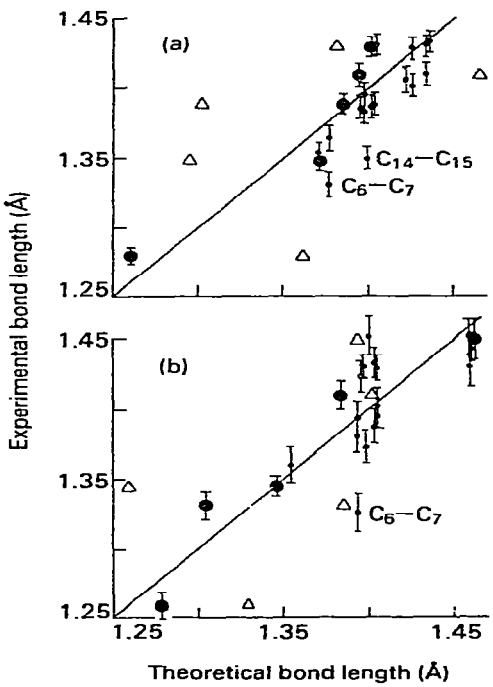


Fig. 2. X-ray bond lengths of nitro derivatives compared to SCF–MO interatomic separations of the parent compounds. (a) **1(NO$_2$)** versus **1(H)–a** (dots) or **1(H)–h** (triangles); (b) **2(NO$_2$)** versus **2(H)–h** (dots) or **2(H)–a** (triangles). Big dots and triangles represent the five most characteristic bonds along the $C_{11}\cdots N_{20}(O_{20})$ path. The straight lines are drawn at 45°.

Based on Grainger and McConnell's data[14] the hydrazone structure has been assigned previously to **2(NO$_2$)** in the crystalline state by comparing its bond lengths with those of structurally related compounds empirically.[22] As can be seen from Table 4 and Fig. 2b, there is an excellent correlation between the observed data and the calculated hydrazonic structure **2(H)–h**, particularly along the $C_{11}\cdots O_{20}$ path ($r = 0{\cdot}956$). At the same time the correlation with the azo form **2(H)–a** is poor in this region ($r = 0{\cdot}503$). Excepting bond C_6—C_7 which was noted to be unusually short[14] according to experimental findings (1·326 Å) and bond C_7—C_8 which is too long (1·451 Å), the X-ray distances fit those calculated for the hydrazone within about 0·03 Å over the entire molecule.

It is interesting to note that in both dyes the measured C_6–C_7 distance is

TABLE 4

BOND LENGTHS INVOLVING NON-HYDROGEN ATOMS OF **2(NO$_2$)** FROM CRYSTAL STRUCTURE DETERMINATION[a] AND THOSE OF THE PARENT **2(H)** TAUTOMERIC PAIR FROM SCF–MO CALCULATIONS

Bond	**2(NO$_2$)**	**2(H)–a**	**2(H)–h**
Hydrazone group			
C(1)–N(17)	1·331(10)[b]	1·385(+54)[c]	1·304(−27)[c]
N(17)–N(18)	1·345(7)	1·259(−86)	1·346(+1)
N(18)–C(11)	1·410(10)	1·401(−9)	1·383(−27)
Naphthalene group			
C(2)–O(20)	1·259(10)	1·329(+70)	1·278(+19)
C(1)–C(2)	1·449(14)	1·393(−56)	1·462(+13)
C(2)–C(3)	1·451(13)	1·431(−20)	1·459(+8)
C(3)–C(4)	1·360(13)	1·371(+11)	1·354(−6)
C(4)–C(5)	1·430(14)	1·431(+1)	1·459(+29)
C(5)–C(6)	1·433(11)	1·425(−8)	1·403(−30)
C(6)–C(7)	1·326(14)	1·375(+49)	1·393(+67)
C(7)–C(8)	1·451(13)	1·420(−31)	1·400(−51)
C(8)–C(9)	1·380(11)	1·375(−5)	1·393(+13)
C(9)–C(10)	1·388(13)	1·424(+36)	1·403(+15)
C(10)–C(1)	1·443(9)	1·433(−10)	1·460(+17)
C(10)–C(5)	1·429(9)	1·403(−26)	1·404(−25)
Benzene group			
C(11)–C(12)	1·402(13)	1·400(−2)	1·404(+2)
C(12)–C(13)	1·423(11)	1·396(−27)	1·395(−28)
C(13)–C(14)	1·429(9)	1·396(−33)	1·396(−33)
C(14)–C(15)	1·373(12)	1·398(+25)	1·398(+25)
C(15)–C(16)	1·394(12)	1·394(0)	1·393(−1)
C(16)–C(11)	1·395(9)	1·402(+7)	1·405(+10)
Nitro group			
C(14)–N(19)	1·482(10)		
N(19)–O(21)	1·217(12)		
N(19)–O(22)	1·223(10)		

[a] From ref. 14. The reported N(18)–O(20) distance is 2·472(11) Å. The crystal referred to was termed the α-modification.[31]

[b,c] Estimated standard deviations ([b]) and differences between calculated and determined bond lengths ([c]) in the last significant figures are given in parentheses.

unreasonably short whereas in most other reported phenylazonaphthol dyes, including some Naphthol AS types, 'normal' C_6—C_7 bond lengths (1·37–1·39 Å) have been observed.[23–30] At the present no explanation can be offered for this anomaly.

4. EMPIRICAL BOND LENGTH CORRELATIONS

This second approach utilizes the vast body of empirical bond dimensions, mostly derived from X-ray diffraction data. Previous authors compared the obtained bond lengths along the crucial path, like the present $C_{11}\cdots X_{20}$ region, with accepted lengths of CN, NN and CO single and double bonds[30] accessible from standard crystallographic tables[32] or alternatively with bond distances found in a few closely related compounds whose structure was unambiguously established (for example, ref. 22). To the best of our knowledge no such data compilation exceeding half a dozen reference structures has been published up to now. To remedy this situation we present in Tables 5 and 6 over 70 entries pertinent to bond dimensions between sp^2 hybridized carbon and nitrogen atoms of the azo or hydrazone chain. We shall focus our attention on two parameters, R(NN) and ΔR(CN), denoting the distance between the nitrogen atoms of the central bond and the difference in the bond lengths of the adjacent carbon–nitrogen linkages. They will prove useful in azo–hydrazone structure discrimination.

Compounds confined to the azo form by the absence of conjugating protic donor substituents[2] are listed in Table 5 together with potentially tautomeric species with established azo preference. The latter are marked with a dagger. Purely hydrazonic or tautomeric but reportedly hydrazonic structures (also marked†) are shown in Table 6. To identify the pertinent polymorph and to facilitate judgement of data quality, space group symbols, R-indices and estimated standard deviations (e.s.d.; in parentheses) have been added to the tables.

The plots in Fig. 3 and the bond length ranges in Table 7 are derived from these data; a few entries had to be omitted on account of low accuracy (e.s.d. $>0{\cdot}05$ Å or R-index $>0{\cdot}15$) or because mixed tautomeric crystal lattice has been assumed for them. For the former reason points 17, 35, 39, 41, 62, and for the latter points 31B and 32B, were excluded. Considering entry 31, two crystallographically independent molecules (A and B) have been reported and the presence of both tautomers in both molecules was claimed.[33] The data of molecule A fit into the azo range whereas those of molecule B are contradictory: its R(NN) is too long (1·306 Å) for the azo form while the ΔR(CN) is too small (0·019 Å) for the hydrazone tautomer. The prototropic hydrogen was found to be closer to the oxygen (O—H: 1·17; N—H: 1·50 Å) but again, the OH distance shows an anomalous extension compared to the standard value (0·99 Å).[32] A similar situation is encountered for point 32.[34]

TABLE 5

BOND LENGTHS BETWEEN sp^2 HYBRIDIZED CARBON AND NITROGEN ATOMS OF THE AZO LINKAGE[a]

No.	*Compound*		*R(C—N)*		*R(N=N)*	*R-index*	*Space group*
1	trans-*Azobenzene*:		1·434(3)		1·247(3)	0·069	$P2_1/a$
2	,4,4′-dimethyl		1·433		1·244	0·102	$P2_1/a$
3	,2,2′-dichloro		1·432(7–10)		1·254(7–10)	0·087	$P2_1/a$
4	,4,4′-dichloro		1·443(5)		1·252(5)	0·049	$P2_1/c$
5	,4,4′-diethoxy		1·421	1·431	1·255	0·086	$P2_1/c$
6	,2,2′-dimethyl-5,5′-diisopropyl		1·423(3)		1·246(4)	0·079	*Pbca*
7	,2,2′,4,4′,6,6′-hexanitro	A	1·426(5)		1·244(5)	0·063	$P2_1/c$
8		B	1·438(5)		1·243(5)	0·047	$P2_1/a$
9	,2-thiocyanato		1·428(9)	1·423(9)	1·261(8)	0·054	$P2_12_12_1$
10	,2-thiocyanato		1·44(2)	1·43(3)	1·22(2)	0·15	$P2_12_12_1$
11	,4-dimethylamino-2′-carboxylic acid		1·385(8–12)	1·421(8–12)	1·269(8–12)	0·093	$P\bar{1}$
12	,4-dimethylamino-4′-sulphonate sodium salt[b]		1·407(6–9)	1·440(6–9)	1·244(6–9)	0·049	$P2_1/c$
13†	,4-amino-2′,3-dimethyl		1·413(4)	1·402(4)	1·258(4)	0·068	$P2_1/a$
14	,4-ethoxy-4′-valerate		1·416(8)	1·409(8)	1·239(7)	0·12	$P\bar{1}$
15	,4-phenylazo		1·461(3·5–5)	1·449(3·5–5)	1·232(3·5–5)	0·078	$P2_1/c$
16	,4-[*N*-(*p*-methoxy)benzylidenamino]	A	1·45(4)	1·43(4)	1·22(5)	0·126	$P2_1/c$
17		B	1·55(6)	1·48(6)	1·09(7)		
	trans-*Phenylazo*-:						
18	tribenzoylmethane		1·443(5)		1·233(4)	0·047	$P2_1/c$
19	2′-(1′,3′-diphenyl-*cis*-propene)		1·476	1·410	1·257	0·122	$P2_1$
20	2′-(1′,3′-diphenyl-*trans*-propene)		1·435	1·417	1·280	0·122	$P2_1/a$
21	3′-(5′-diethylamino-4′-methyl-1-phenylpyrazole)		1·429(5)	1·408(5)	1·258(4)	0·053	$P2_1/c$
22	5′-(3′-phenyl-2-pyrrolidino-spiro [1H-indene-1,2′(3′*H*)-[1,3,4]thiadiazole])		1·43(1)	1·37(1)	1·26(1)	0·091	$P2_1/c$
23	3′-(4a′,5′,6′,7′,8′,8a′-hexahydro-7′-methyl-4a′-morpholino-4′-phenyl-1*H*-pyrido[4′,4′-*e*]-[1′,3′,4′]thiadiazine)		1·427(6)	1·401(6)	1·266(5)	0·072	$P2_1/n$

	trans-*4-Bromophenylazo-*:						
24	1′-(1′-benzoyl-2′-benzoyloxy-2′-phenylethylene)		1·448(10)	1·401(10)	1·279(8)	0·099	$P\bar{1}$
	trans-*2-Methoxyphenylazo-*:						
25	1′-(1′-hydroperoxy-2′-phenylcyclohexane)		1·41(1)		1·28(1)	0·10	$P2_1/c$
26	*Bis*-trans-*phenylazo-α,β*-trans-*stilbene*		1·432(*av.*)	1·410(*av.*)	1·252(*av.*)	0·109	$P2_1/c$
	trans-*1,1′-Azobis-*:						
27	[4-bromobenzaldehyde]bis[*O*-carboxyoxime]diethyl ester		1·49(1)		1·22(1)	0·07	$P\bar{1}$
28	-[4,-bromobenzaldehyde]bis[*O*-carboxy-oxime]diethyl ester		1·47(1)		1·20(1)	0·07	$P2_1/a$
29	carboxamide		1·483(1)		1·228(2)		
30†	trans-*1′-(4-iodocyclohexylazo)-2′-naphthol*		1·43(5)	1·44(5)	1·21(5)	0·124	$P2_1/c$
	trans-*1′-(2-Thiazolylazo)-*:						
31†	2′-naphthol	A	1·382(7)	1·371(7)	1·278(6)	0·051	$P2_1/a$
		B	1·378(7)	1·359(7)	1·306(6)		
32†	6′-bromo-2′-naphthol	A	1·41(2)	1·39(2)	1·28(2)	0·064	$P2_12_12_1$
		B	1·35(2)	1·33(2)	1·31(2)		
33†	trans-(*4-Hydroxyphenylazo*)*uracil*		1·401(5)	1·411(5)	1·265(5)	0·052	$I4_1/a$

[a] A and B denote crystallographically independent molecules in the same crystal.

[b] Monohydrate, monoethanolate.

† Formally tautomeric but predominantly azo structure.

References corresponding to the no. in the first column: (1) C.J. Brown, *Acta Crystallogr.*, **21**, 146 (1966). (2) *Idem, ibid.*, **21**, 153 (1966). (3) M. Komeyama, S. Yamamoto, N. Nishimura and S. Hasegawa, *Bull. Chem. Soc. Jap.*, **46**, 2606 (1973). (4) H. Hope and D. Victor, *Acta Crystallogr., Sect. B*, **25**, 1849 (1969). (5) J. L. Galigné, *ibid.*, **26**, 1977 (1970). (6) J. B. Wetherington, K. D. Holmes, Jr and J. W. Moncrief, *ibid.*, **30**, 246 (1974). (7, 8) E. J. Graeber and B. Morosin, *ibid.*, **30**, 310 (1974). (9) S. M. Aldoshin, O. A. D'yachenko and L. O. Atovmyan, *Zh. Strukt. Khim.*, **18**, 1042 (1977). Engl. transl. **18**, 827 (1977). (10) K. K. Kakati and B. Chaudhuri, *Acta Crystallogr., Sect. B*, **24**, 1645 (1968). (11) D. Moreiras, J. Solans, X. Solans, C. Miravitlles, G. Germain and J. P. Declercq, *Cryst. Struct. Comm.*, **9**, 921 (1980). (12) A. W. Hanson, *Acta Crystallogr., Sect. B*, **29**, 454 (1973). (13) S. Kurosaki, S. Kashino and M. Haisa, *ibid.*, **32**, 3160 (1976). (14) J. S. Prasad, *ibid.*, **35**, 1407 (1979). (15) R. D. Giraldi and I. L. Karle, *ibid.*, **28**, 1635 (1972). (16, 17) G. V. Vani and K. Vijayan, *ibid.*, **33**, 2236 (1977). (18) D. B. Pendergrass, Jr, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, **94**, 8722 (1972). (19, 20) E. F. Serantoni, L. R. di Sanseverino and G. Rosini, *J. Chem. Soc., Sect. B*, 2372 (1971). (21–23) G. V. Boyd, T. Norris and P. F. Lindley, *J. Chem. Soc. Perkin Trans. I*, 1673 (1976). (24) D. B. Pendergrass, Jr. D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, **94**, 8722 (1972). (25) S. Bozzini, S. Gratton, A. Risaliti, A. Stener, M. Calligaris and G. Nardin, *J. Chem. Soc. Perkin I*, 1377 (1977). (26) J. P. Chesick, *Acta Crystallogr., Sect. B*, **29**, 2309 (1973). (27, 28) K. T. Go and G. Kartha, *J. Cryst. Mol. Struct.*, **5**, 149 (1975). (29) D. T. Cromer, A. C. Larson and R. F. Stewart, *J. Chem. Phys.*, **65** 336 (1976). (30) S. G. Biswas and A. Mukherjee, *Acta Crystallogr., Sect. B*, **32**, 2230 (1976). (31) M. Kurahashi, *Bull. Chem. Soc. Jap.*, **49**, 2927 (1976); *Chem. Lett.*, 181 (1974). (32) M. Kurahashi, M. Fukuyo, A. Shimada and A. Kawase, *Bull. Chem. Soc. Jap.*, **49**, 872 (1976); M. Kurahashi, A. Kawase, K. Hirotsu, M. Fukuyo and A. Shimada, *ibid.*, **45**, 1940 (1972). (33) C. L. Coulter and N. R. Cozzarelli, *Acta Crystallogr., Sect. B*, **30**, 2176 (1974).

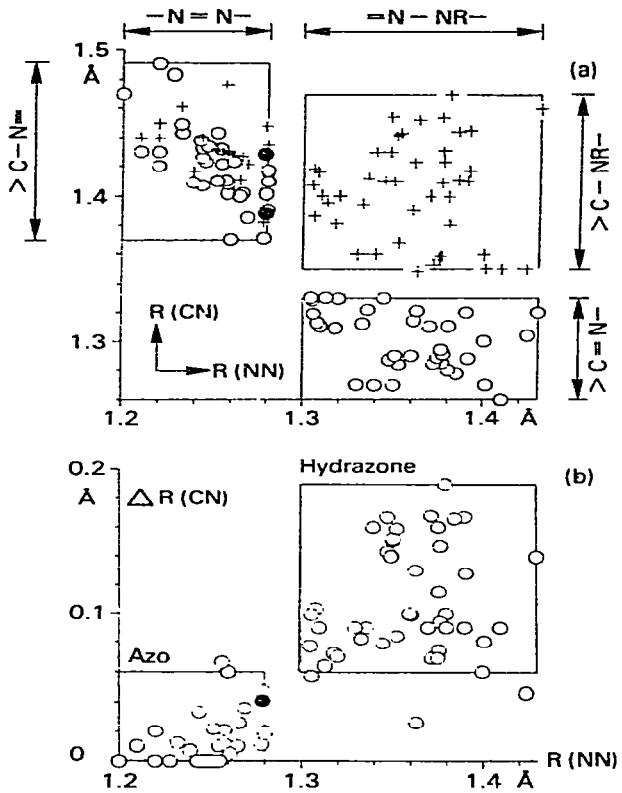


Fig. 3. (a) Areas representing CN and NN bond length ranges of the azo (points 1–33, top left) and the hydrazone linkage (points 34–73, top and bottom right). Data from Tables 5–6. In asymetrical structures the shorter CN bond is shown by an empty circle, the longer one by a cross. (b) ΔR(CN) vs R(NN) plot from the same data. The frames enclose azo (left) and hydrazone (right) structures as above. For points outside these areas cf. text. The shaded symbol denotes I(NO_2) from this work in both diagrams.

For two hydrazones ΔR(CN) is significantly smaller than the lower limit (0·06 Å) deduced for this type. It can be traced back to the CN single bond, which appears to be extremely short as a result of strong conjugation with the *p*-nitrophenyl (point 42) or α,α-dicyanovinyl group (point 57). In other nitrophenylhydrazones (points 41, 43–47, 58–61, 68–69) such an anomaly was not observed. Similarly, in two azo structures ΔR(CN) exceeds the upper limit for the azo types (0·06 Å) due to non-planarity of the molecule in one case (point 19) and to disorder in the other (point 17, not shown in Fig. 3b). These few exceptions, however, do not seriously limit the utility of this parameter.

It has to be borne in mind that such compilations depend critically on the number and variety of molecular structures used in their evaluation. Previously established

TABLE 6

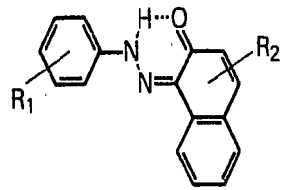
BOND LENGTHS BETWEEN sp^2 HYBRIDIZED CARBON AND NITROGEN ATOMS OF THE HYDRAZONE LINKAGE[a]

No.	*Compound*		*R(C—N)*	*R(N=N)*	*R(C=N)*	*R-index*	*Space group*
	N-*Phenylhydrazone of:*						
34	2-oxopropionaldehyde		1·423(10)	1·361(10)	1·314(11)	0·129	$P2_1/c$
35	iodocyanomethanone		1·46(6)	1·31(6)	1·22(6)	0·138	$Pn2_1a$
36	2-(indan-1,2,3-trione)[b]		1·418(4)	1·306(4)	1·319(4)	0·053	$P2_12_12_1$
	Bis-N-*phenylhydrazone*:						
37	1,2,4-trithiolane-3,5-dione		1·41(0·7–1·1)	1·35(0·7–1·1)	1·27(0·7–1·1)	0·056	$C2/c$
	N-(*4-Bromophenyl*)*hydrazone of:*						
38	ribose		1·46(3–4)	1·43(3–4)	1·32(3–4)	0·14	$P2_12_12_1$
39	arabinose		1·42(3–8)	1·38(3–8)	1·36(3–8)	0·08	$P2_1$
40	*cis*-5-acetyl-5,5a,6,7,8,10,11,11a-octahydro-9*H*-cyclooct[*b*]indol-9-one		1·385(3)	1·377(3)	1·291(3)	0·057	$P\bar{1}$
	N-(*3-Nitrophenyl*)*hydrazone of:*						
41	acetone		1·351(8)	1·417(7)	1·273(9)	0·169	$C2/c$
	N-(*4-Nitrophenyl*)*hydrazone of:*						
42	acetone		1·350(6)	1·424(6)	1·304(13)	0·109	$P2_1/c$
43	4-dimethylaminobenzaldehyde·HCl	A	1·36	1·40	1·30	0·08	$P\bar{1}$
44		B	1·41	1·39	1·32		
	N-(*2,4-Dinitrophenyl*)*hydrazone of:*						
45	4-methylbenzophenone		1·353(4)	1·372(4)	1·284(4)	0·05	$P2_1/c$
46	tetracyclo[5,2,1,$0^{2,6}$,$0^{4,9}$]decane-3-one		1·350(3)	1·401(2)	1·270(3)	0·059	$P\bar{1}$
	N-(*2,4-Dinitro-6-bromophenyl*)*hydrazone of:*						
47	(4S)-2-(prop-2-enyl)rethron-4-yl(1*R*,3*R*)-chrysanthemate		1·35(5)	1·41(5)	1·26(5)	0·0885	$P2_1$

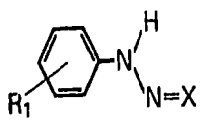
(continued)

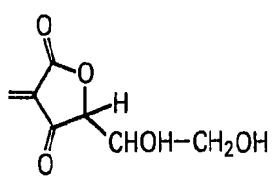
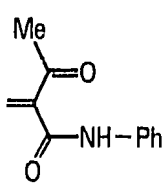
TABLE 6—*contd.*

No.	*Compound*		*R(C—N)*	*R(N=N)*	*R(C=N)*	*R-index*	*Space group*
	N-*Benzoyl*-N-*phenylhydrazone of*:						
48	2-(indan-1,2,3-trione)		1·431(3) 1·423(3)	1·377(2)	1·284(3)	0·063	$P2_1/c$
49	2-(indan-1,2,3-trione)[b]		1·444(4) 1·411(5)	1·385(5)	1·278(5)	0·053	$P2_12_12_1$
50	2-(1,3-diphenylpropanetrione)		1·43(1) 1·36(2)	1·34(1)	1·27(1)	0·083	$Pna2_1$
	N-*Benzoyl*-N-(*4-bromophenyl*)*hydrazone of*:						
51	2-(1,3-diphenylpropanetrione)		1·47(1) 1·38(1)	1·38(1)	1·28(1)	0·066	$Pna2_1$
	N-(*4-Bromobenzoyl*)-*N-phenylhydrazone of*:						
52	2-(indan-1,2,3-trione)	A(*syn*)	1·430(8) 1·454(9)	1·348(8)	1·287(8)	0·081	$P\bar{1}$
53		B (*anti*)	1·442(9) 1·441(9)	1·351(8)	1·290(8)		
	N-(*4*-tert-*Butylbenzoyl*)-N-*phenylhydrazone of*:						
54	2-(indan-1,2,3-trione)		1·445(4) 1·417(4)	1·391(4)	1·288(5)	0·071	$P\bar{1}$
55	2-(indan-1,2,3-trione) acetone solvate		1·454(6) 1·409(6)	1·376(5)	1·294(7)	0·090	$P2_1/c$
	N-(*4-Chlorophenyl*)-N-(*2,2-dicyanovinyl*)*hydrazone of*:						
56	dicyanomethanone	A	1·443(7) 1·368(6)	1·353(6)	1·284(7)	0·043	$P2_1/c$
57		B	1·452(7) 1·348(7)	1·363(6)	1·322(8)		



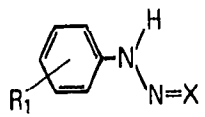
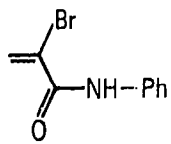
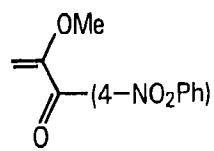
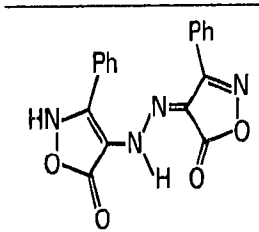
	R_1	R_2					
58†	4-NO_2	H	1·410(10)	1·345(7)	1·331(10)	0·13	*Pb*
59†	2-NO_2-4-Me	H	1·381(5)	1·318(6)	1·309(5)	0·078	$P2_1/a$
60†	2-NO_2-4-Cl	H	1·395(10)	1·313(10)	1·331(10)	0·112	$P2_1/c$
61†			1·394(7)	1·333(6)	1·312(6)	0·057	$P2_1/c$
62†	2,5-di-Cl	3-CONH-Ph	1·46(5)	1·19(4)	1·33(5)	0·153	$P2_1/c$
63†	2,5-di-Cl	3-CONH(2-MeO-4-Cl-Ph)	1·412(10)	1·336(8)	1·322(9)	0·0804	$P2_12_12_1$
64†	2,5-di-Cl	3-CONH(2,5-di-MeO-4-Cl-Ph)	1·40(1)	1·32(1)	1·33(1)	0·103	$P\bar{1}$
65†	2-COO(*n*-Bu)	3-CONH(5-benzimidazolin-2-one)	1·407(5)	1·305(5)	1·330(5)		$P\bar{1}$
66†	4-Br	3,4-CH(Me_2)-CHMe-O-	1·40(1)	1·31(1)	1·31(1)	0·054	$P\bar{1}$

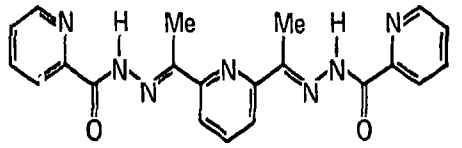


	R_1	X					
67†	4-Br		1·416(8)	1·308(8)	1·313(8)	0·042	$P2_12_12_1$
68†	2-NO_2-4-Cl		1·36(2)	1·33(2)	1·27(2)	0·12	$P2_1/c$

(continued)

TABLE 6—*contd.*

No.	*Compound*	*R(C—N)*	*R(N=N)*	*R(C=N)*	*R-index*	*Space group*
						
	R_1 *X*					
69†	2-NO_2-4-Me 	1·39(3)	1·36(3)	1·29(3)	0·099	$P2_1/a$
70†	2-$PhSO_2$-4-Cl 	1·40	1·38(~3)	1·31		
71†		1·40(1–2)	1·37(1–2)	1·31(1–2)	0·083	$P2_1/c$
72†		1·386(3)	1·306(3)	1·329(3)	0·047	$C2/c$

73†		1·357(5) 1·359(4)	1·375(4) 1·376(4)	1·288(5) 1·285(4)	0·066	*C2/c*

[a] A and B denote crystallographically independent molecules in the same crystal.
[b] 1:1 Complex of entries 36 and 49.

† Formally tautomeric but predominantly hydrazone structure. References corresponding to the no. in the first column: (34) R. C. Secconbe and C. H. L. Kennard, *Aust. J. Chem.*, **23**, 395 (1970). (35) M. Bukowska-Strzyzewska and J. Skoweranda, *Cryst. Struct. Comm.*, **5**, 727 (1976). (36) J. A. McMillan, D. Y. Curtin and I. C. Paul, *Acta Crystallogr., Sect. B*, **34**, 2878 (1978). (37) G. Casalone and A. Mugnoli, *J. Chem. Soc., Sect. B*, 415 (1971). (38) K. Bjåmer, S. Furberg and C. S. Petersen, *Acta Chem. Scand.*, **18**, 587 (1964). (39) S. Furberg and C. S. Petersen, *ibid.*, **16**, 1539 (1962). (40) D. J. Duchamp and C. G. Chidester, *Acta Crystallogr., Sect. B*, **28**, 1092 (1972). (41) Gy. Menczel, *Acta Chim. Acad. Sci. Hungar.*, **62**, 41 (1969). (42) Gy. Menczel, G. Samay and K. Simon, *ibid.*, **72**, 441 (1972). (43, 44) A. L. Anderson and J. N. Brown, *Cryst. Struct. Comm.*, **5**, 197 (1976). (45) Y. Takada, M. Tabata, A. Suzuki and A. Furusaki, *Chem. Lett.*, 269 (1975). (46) J. Potenza, D. Mastropaolo, D. Gallaher and T. Henderson, *Acta Crystallogr., Sect. B*, **31**, 1975 (1975). (47) M. J. Begley, L. Crombie, D. J. Simmonds and D. A. Whiting, *J. Chem. Soc. Perkin Trans. I*, 1230 (1974). (48) S. A. Puckett, M. K. Greensley, I. C. Paul and D. Y. Curtin, *J. Chem. Soc. Perkin Trans. II*, 847 (1977). (49) Ref. 36 above. (50, 51) D. B. Pendergrass, Jr, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.*, **94**, 8730 (1972). (52, 53) Ref. 48 above. (54) R. A. Booker, D. Y. Curtin and I. C. Paul, *Acta Crystallogr., Sect. B*, **34**, 2882 (1978). (55) S. A. Puckett, I. C. Paul and D. Y. Curtin, *J. Chem. Soc. Perkin Trans. II*, 1873 (1976). (56, 57) F. L. May, D. J. Dahm, H. C. Berk and J. E. Franz, *Cryst. Struct. Comm.*, **8**, 487 (1979). (58) C. T. Grainger and J. F. McConnell, *Acta Crystallogr., Sect. B*, **25**, 1962 (1969). (59) A. Whitaker, *Z. Kristallogr.*, **147**, 99 (1978). (60) *Idem, ibid.*, **145**, 271 (1977). (61) L. J. Guggenberger and G. Teufer, *Acta Crystallogr., Sect. B*, **31**, 785 (1975). (62) A. Whitaker, *Z. Kristallogr.*, **146**, 173 (1977). (63) D. Kobelt, E. F. Paulus and W. Kunstmann, *ibid.*, **139**, 15 (1974). (64) *Idem, Acta Crystallogr., Sect. B*, **28**, 1319 (1972). (65) E. F. Paulus and K. Hunger, *Farbe Lack*, **86**, 116 (1980). (66) R. G. Cooke, C. L. Raston and A. H. White, *Aust. J. Chem.*, **33**, 441 (1980). (67) J. Hvoslef and S. Nordenson, *Acta Crystallogr., Sect. B*, **32**, 448 (1976). (68) H.-C. Mez. *Ber. Bunsenges. Phys. Chem.*, **72**, 389 (1968). (69) C. J. Brown, *J. Chem. Soc., Sect. A*, 405 (1967). (70) W. Jeblick and K. Schank, *Ann. Chem.*, 1727 (1976). (71) R. Hoge and K. F. Fischer, *Cryst. Struct. Comm.*, **4**, 509 (1975). (72) B. Bovio and S. Locchi, *J. Cryst. Mol. Struct.*, **8**, 149 (1979). (73) C. Pelizzi and G. Pelizzi, *Acta Crystallogr., Sect. B*, **35**, 126 (1979).

ranges were considerably narrower and lead sometimes to conflicts in tautomer assignment, for example in the case of the *p*-bromophenylhydrazone of dunnione (point 66) where the position of the prototropic hydrogen suggested the hydrazone structure[29] whereas the CN and NN distances were significantly outside the range considered to be valid for the hydrazone.[22] They do fit, however, into the present limits and in particular the large ΔR(CN) value (0·09 Å) is strongly indicative of a hydrazone structure.

This result can easily be rationalized on quantum chemical grounds. An electron donor substituent, like the alicyclic ether group in dunnione, increases the hydrazone preference if attached to the 4-position of a 1-phenylazo-2-naphthol dye even more substantially than does an electron acceptor group (e.g. carbonamide in Naphthol AS) in position 3 (cf. Fig. 4 in ref. 2). All the Naphthol AS type dyes whose crystal structures have been reported (points 62–65) exhibit a hydrazone predominance in full agreement with previous theoretical estimates.[2]

Returning to our main subject, a comparison with Table 7 shows that the observed bond lengths for **1**(NO_2) (CH: 1·388 and 1·428; NN: 1·279 Å) are only compatible with the azo tautomer.

TABLE 7

SUMMARY OF BOND DISTANCES (Å) INVOLVED IN THE AZO OR HYDRAZONE LINKAGE

Azo structure	*Hydrazone structure*
$1·37 < R(C—N) < 1·49$	$1·35 < R(C—N) < 1·47$
$1·20 < R(N=N) < 1·28$	$1·30 < R(N—N) < 1·43$
	$1·26 < R(C=N) < 1·33$
$0·00 < \Delta R(CN) < 0·06$	$0·06 < \Delta R(CN) < 0·19$

As conjugating terminal substituents tend to shorten the CN bond of an azo group and increase at the same time the NN distance, some sort of inverse relationship between these bonds is generally assumed. Such a trend is indeed recognizable from Fig. 3a, particularly for the shorter of the two CN bonds which are most affected by the substituents. The corresponding points in **1**(NO_2) lie close to the lower right limits displayed for the azo form in Fig. 3a as expected for a strong interaction between the amino and the nitro groups across the azo linkage.

The bond dimensions of **2**(NO_2) (C—N: 1·410; C=N: 1·331; N—N: 1·345 Å) fit snugly into the hydrazonic structure range of Table 7, thus confirming empirical deductions of previous authors.[22,30]

The difference between the C_{11}–N_{18} and C_1—N_{17} bond lengths (0·079 Å) in **2**(NO_2) is about twice the splitting (0·040 Å) obtained for the same bonds in **1**(NO_2), which again supports the above assignment for both compounds.

A final piece of evidence, strongly suggestive of the azo predominance in **1**(NO_2) is the position of the mobile proton, H_{20B}. Its attachment to the amine nitrogen,

N_{20}, is highly significant, as follows from a comparison of the N_{20}–H_{20B} and N_{18}–H_{20B} distances (1·04 and 1·89 Å with an e.s.d. of 0·05 Å).

Concluding this section, the azo structure for **1**(NO_2) and the hydrazone form for **2**(NO_2) seem now to be convincingly established in the crystalline state. This is the first time to our knowledge that both theoretical calculations and empirical correlations with X-ray data were used to elucidate the tautomeric structure of an azo dye in the crystal.

5. MOLECULE AND CRYSTAL STRUCTURES IN **1**(NO_2)–DIOXANE 2:1 SOLVATE

Further geometric properties of the dye molecule **1**(NO_2) are collected in Tables 8–11.

The non-hydrogen skeleton of the dye molecule is fairly planar and of *trans* configuration. The nitro group is twisted out of the molecular plane most significantly. In the strict crystallographic sense, however, the molecule has to be classified as non-planar due to deviations exceeding 3σ, where σ (0·006 Å) represents the estimated standard deviation from the best plane.[35] Table 10 lists some of the torsional angles about the azo bond and Table 11 shows the out-of-plane distances from the least-squares plane of the molecule. Parts of the molecule, like the naphthalene ring (A), the CNNC chain (B), the benzene ring (C) and the C—NO_2 fragment (D), can nevertheless be fitted to least-squares planes with an accuracy satisfying even the crystallographic criterion. Twist angles between these planes are: 3·0° (A/B), 1·5° (A/C), 7·6° (A/D), 1·5° (B/C), 5·3° (B/D) and 6·3° (C/D). For comparison, an A/C angle of 9° and a C/D angle of 5° has been reported for **2**(NO_2).[14] Accordingly, **1**(NO_2) is more planar on account of the smaller inclination between the planes of the naphthalene and benzene rings, whereas the nitro group is somewhat less twisted in **2**(NO_2), probably as a consequence of its stronger conjugation with the amine type nitrogen of the hydrazone linkage.

Considering the average separations between two hydrogen bonded nitrogens (3·1 ± 0·13 Å)[36] the distance between N_{18} and N_{20} is too short for a non-bonded pair of atoms. This suggests an N—H···N bond in **1**(NO_2) forming a six-membered

TABLE 8

INTERATOMIC SEPARATIONS (Å) AND THEIR ESTIMATED STANDARD DEVIATIONS INVOLVING HYDROGEN ATOMS IN **1**(NO_2)–DIOXANE 2:1 SOLVATE

C(3)–H(3)	1·09(5)	C(9)–H(9)	1·06(5)
C(4)–H(4)	1·05(5)	C(12)–H(12)	1·06(5)
C(6)–H(6)	1·08(5)	C(13)–H(13)	1·10(5)
C(7)–H(7)	1·02(5)	C(15)–H(15)	1·04(5)
C(8)–H(8)	1·04(5)	C(16)–H(16)	1·05(5)
N(20)–H(20A)	0·98(5)	N(18)–H(20B)	1·89(5)
N(20)–H(20B)	1·04(5)	O(23)[a]–H(20A)	2·14(5)

[a] Nearest dioxane oxygen. The dioxane C–H bond lengths are: 1·01(5), 1·02(5), 1·13(5) and 1·18(5) Å.

TABLE 9

BOND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FROM THE CRYSTAL STRUCTURE DETERMINATION OF I(NO_2)–DIOXANE 2:1 SOLVATE

Azo group		*Benzene group*	
C(10)—C(1)—N(17)	113·9(5)	C(16)—C(11)—C(12)	122·5(5)
C(2)—C(1)—N(17)	124·7(5)	C(11)—C(12)—C(13)	117·9(5)
C(1)—N(17)—N(18)	119·4(4)	C(12)—C(13)—C(14)	118·2(5)
N(17)—N(18)—C(11)	112·5(4)	C(13)—C(14)—C(15)	124·3(5)
N(18)—C(11)—C(12)	123·1(5)	C(14)—C(15)—C(16)	118·2(5)
N(18)—C(11)—C(16)	114·4(5)	C(15)—C(16)—C(11)	119·0(5)
	Naphthalene group		
C(1)—C(2)—N(20)	123·6(5)	C(5)—C(10)—C(1)	118·2(5)
N(20)—C(2)—C(3)	118·0(5)	C(10)—C(5)—C(6)	117·7(5)
C(10)—C(1)—C(2)	121·3(5)	C(5)—C(6)—C(7)	122·2(6)
C(1)—C(2)—C(3)	118·4(5)	C(6)—C(7)—C(8)	119·8(6)
C(2)—C(3)—C(4)	120·7(5)	C(7)—C(8)—C(9)	120·6(6)
C(3)—C(4)—C(5)	122·4(5)	C(8)—C(9)—C(10)	121·1(6)
C(4)—C(5)—C(10)	119·0(5)	C(9)—C(10)—C(5)	118·6(5)
C(4)—C(5)—C(6)	123·3(5)	C(9)—C(10)—C(1)	123·3(5)
	Nitro group		
C(13)—C(14)—N(19)	124·3(5)	C(14)—N(19)—O(22)	114·7(5)
C(15)—C(14)—N(19)	120·9(5)	O(21)—N(19)—O(22)	124·4(4)
C(14)—N(19)—O(21)	120·9(5)		

TABLE 10

SOME TORSIONAL ANGLES[a] (°) ABOUT THE AZO BOND IN I(NO_2)–DIOXANE 2:1 SOLVATE

C(1)—N(17)—N(18)—C(11)	−179·1
C(12)—C(11)—N(18)—N(17)	−1·1
C(16)—C(11)—N(18)—N(17)	−179·1
N(18)—N(17)—C(1)—C(2)	−0·3

[a] As defined by W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

TABLE 11

NON-HYDROGEN ATOM DISTANCES FROM THE LEAST-SQUARES PLANE OF THE DYE MOLECULE[a] IN I(NO_2)–DIOXANE 2:1 SOLVATE

Atom	*Deviation (Å)*	*Atom*	*Deviation (Å)*
C(1)	0·044	C(12)	−0·018
C(2)	0·037	C(13)	−0·002
C(3)	0·031	C(14)	0·002
C(4)	−0·012	C(15)	−0·011
C(5)	−0·017	C(16)	−0·031
C(6)	−0·058	N(17)	0·016
C(7)	−0·060	N(18)	−0·013
C(8)	0·006	N(19)	0·019
C(9)	0·042	N(20)	0·016
C(10)	0·028	O(21)	0·121
C(11)	−0·019	O(22)	−0·123

[a] $0{\cdot}6466\,X - 0{\cdot}5270\,Y - 0{\cdot}5516\,Z = 13{\cdot}0701$ in units of fractional coordinates. The average e.s.d. of the deviations is 0·006 Å.

chelate ring. A better operational criterion for the existence of a hydrogen bond is that at least two heavy atom–hydrogen atom distances shorter by at least 0·2 Å than the sum of van der Waals radii be present.[37] The NH distances (1·04 and 1·89 Å) harmonize with the notion of a hydrogen bond, both being much shorter than the sum of the radii (2·7 Å).

Similarly, the close contact observed between the dioxane oxygen and the N_{20} atom of the dye (3·069 Å) indicates intermolecular hydrogen bonding. This value is in the range of tabulated N—H · · · O distances of amines which have an average of 3·04 ± 0·13 Å.[36] The O · · · H distance (2·14 Å) also favours an H-bond as required by the van der Waals radii (2·6 Å).[37] To each one of the dioxane oxygens a dye molecule is bonded through its H_{20} atom, composing a hydrogen bonded complex in which three molecules participate in a manner illustrated in Fig. 4.

Packing in the crystal of both nitro compounds is compared in Fig. 5, which was drawn for stereoscopic viewing and is self-explanatory.

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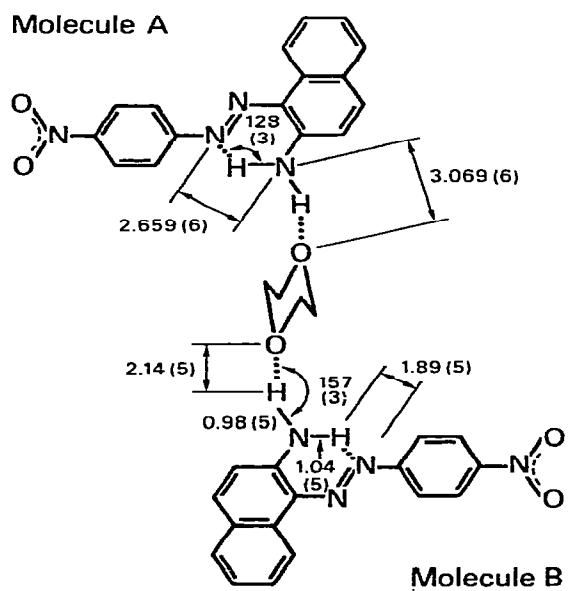

Fig. 4. Schematic diagram showing hydrogen bonding in **1**(NO_2)–dioxane 2:1 solvate. Interatomic separations (Å) and angles (°) are given with their estimated standard deviations in parentheses. The centre of symmetry of the dioxane molecule coincides with an inversion centre of the crystal. The dye molecules A and B lie on parallel planes 3·772 Å apart.

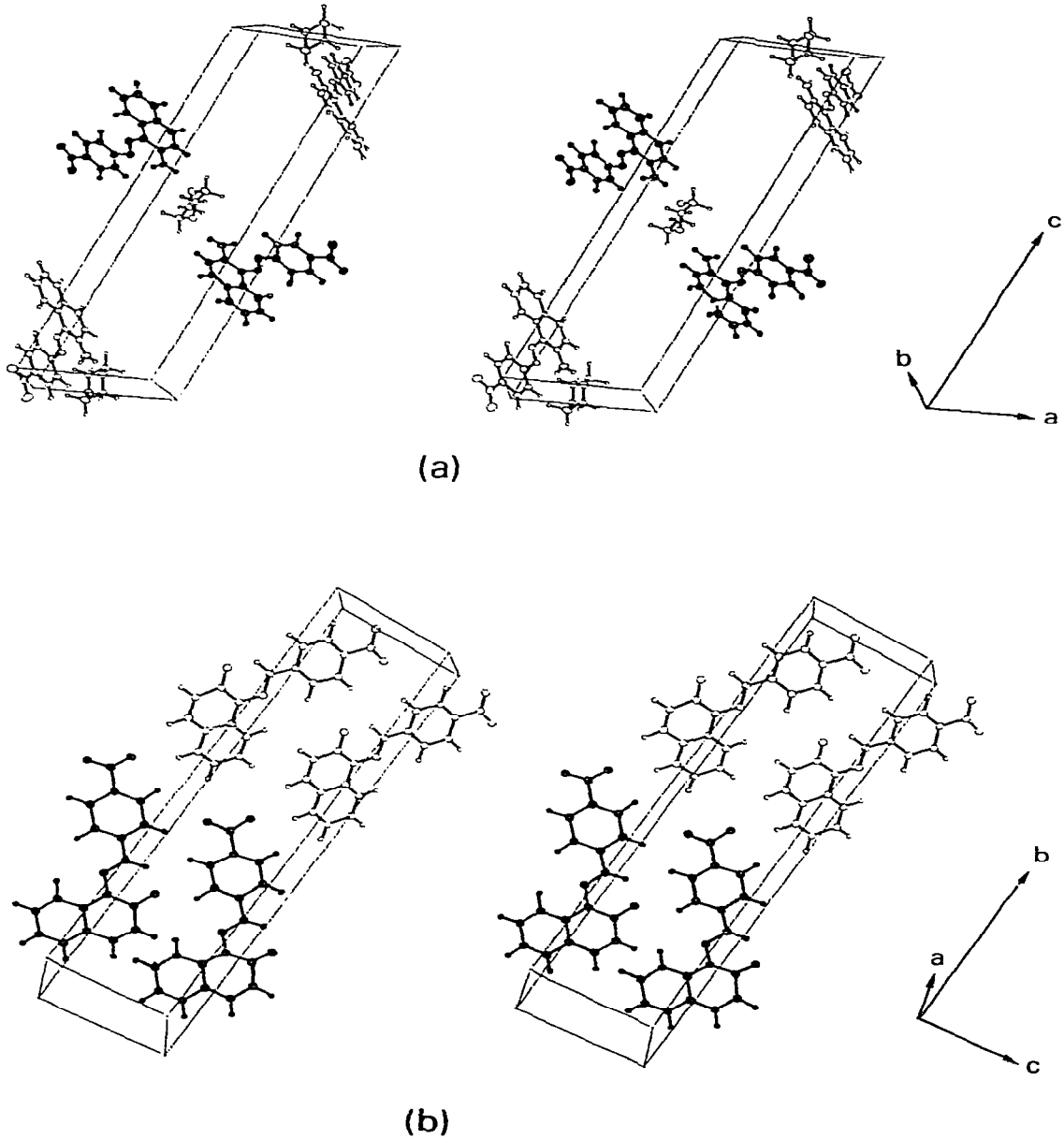

Fig. 5. Stereoscopic view of the crystal packing in the unit cell of (a) **1**(NO_2) and (b) **2**(NO_2). The latter was plotted from published data;[14] its hydrogen atom positions were calculated assuming standard criteria for dimensions. Dye molecules of the same shade lie on parallel planes.

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