The Crystal Structure of 1,2-Naphthoquinone 1-(2-Nitro-4-chlorophenylhydrazone)

By Lloyd J. Guggenberger and Gunter Teufer

Central Research Department and Pigments Department, * *Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware* 19898, *U.S.A.*

The crystal structure of 1,2-naphthoquinone 1-(2-nitro-4-chlorophenylhydrazone) was determined from three-dimensional room-temperature diffractometer data. The frequently used azo name for this compound is 2-nitro-4-chlorophenylazo-2'-naphthol (Parachlor Red). The molecular structure is that of the hydrazone tautomer with a N–N distance of 1·333 (6) Å. The entire molecule is essentially planar except for the NO_2 group which makes an angle of 7·8° with the molecular plane. The molecular planarity is due in part at least to the presence of an intramolecular bifurcated hydrogen bond characterized by 0·88 (8) Å for N–H, 1·95 (3) Å for H···O and 129° for N–H···O. All hydrogen atoms were located and refined. The structure was solved by computer packing techniques in conjunction with intermolecular potential functions. The refinement converged with an R of 0·048 for 1018 reflections with $F > \sigma(F)$. Crystals are monoclinic, space group $P2_1/c$, with $a = 12\cdot923$ (6), $b = 6\cdot964$ (2), $c = 15\cdot781$ (6) Å, and $\beta = 94\cdot27$ (3)° with four molecules per cell.

Introduction

The compound 1,2-naphthoquinone 1-(2-nitro-4-chlorophenylhydrazone) is a red 'azo' pigment frequently identified as 2-nitro-4-chlorophenylazo-2'-naphthol (Parachlor Red). The different names arise from the fact that there are two tautomeric forms possible for this compound, the hydrazone tautomer (I*a*) and the azo tautomer (I*b*).

(I*a*)

(I*b*)
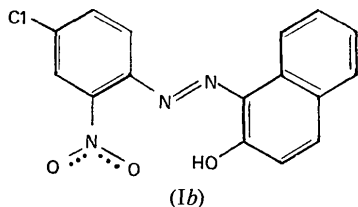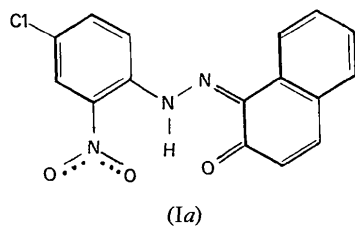
With accurate crystal-structure data now available on azo pigments it seems that many of the hydroxyazo pigments exist, in the solid state at least as hydrazones (Pendergrass, Paul & Curtin, 1972; Kuder, 1972). The crystal structure of the title compound was determined to establish the solid-state valence-bond tautomer, the nature of any intramolecular hydrogen bonding, and the possible existence of unusual intermolecular contacts.

Experimental

The compound is prepared by the coupling of diazotized *p*-chloro-*o*-nitroaniline with 2-naphthol. Crystals suitable for X-ray work were obtained from chloroform. The crystal data are given in Table 1. A prismatic crystal of dimensions $0\cdot03 \times 0\cdot17 \times 0\cdot08$ mm was mounted on a Picker four-circle automatic diffractometer with the *b* axis coincident with the diffractometer φ axis. Copper radiation (Cu $K\alpha = 1\cdot5418$) was used with a nickel filter. Data were measured using the θ–2θ scan technique (1° min⁻¹) with a scan range of 1·0° plus the dispersion. Backgrounds of 20 s were measured before and after each scan. In total 1203 reflections were measured to $90°2\theta$ including $hk0$ and $\bar{h}k0$ data which were averaged.

Table 1. *Crystal data*

Formula: $C_{16}H_{10}N_3O_3Cl$	M.W. 327·71
Crystal system: monoclinic	$D_x = 1\cdot54$ g cm⁻³ ($Z=4$)
$a = 12\cdot923$ (6) Å	$D_m = 1\cdot54$ g cm⁻³
$b = 6\cdot964$ (2)	$F(000) = 672$
$c = 15\cdot781$ (6)	λ(Cu $K\alpha$) = 1·5418 Å
$\beta = 94\cdot27$ (3)°	Space group: $P2_1/c$
$V = 1416\cdot3$ Å³	μ(Cu $K\alpha$) = 25·9 cm⁻¹

The data were corrected for Lorentz and polarization effects but not for absorption. No decomposition correction was necessary. The structure-factor errors were estimated according to a scheme reported earlier (Guggenberger, 1968); reflections with $F < \sigma(F)$ were given zero weight in the refinement.

Considerable effort was expended in trying to solve the structure by Patterson and Patterson superposition techniques after failing with direct methods. It was not possible to establish unequivocally the Cl–Cl vectors in either the Harker plane $(U, \frac{1}{2}, W)$ or Harker line $(0, V, \frac{1}{2})$. In retrospect we see that we had fairly well

established the Cl x and z coordinates indirectly from the Patterson and packing considerations. The Harker line consisted of one large broad peak such that the double-weight Cl–Cl vector could occur anywhere from $\frac{6}{60}-\frac{54}{60}$. There was a minimum in this broad peak at $V=\frac{1}{2}$ which is where the Cl–Cl vector actually occurs. Both sharpened and unsharpened Patterson functions were used in these considerations.

The structure was solved by the packing method of Williams (1969) and the program *PACK5* (Williams, 1964). The Williams quadratic functions were used for C$\cdots$C, C$\cdots$H, and H$\cdots$H intermolecular potentials. The added assumption was made that the C atom potentials would also be adequate for the Cl, N, and O atoms; this is probably not a severe assumption if you are only using the potential functions to solve the phase problem. The correct molecular position was accessible from our first trial position; the packing program converged in a few cycles accompanied by a decrease of about 400 kcal mol^{-1} in the packing energy.

The model derived from *PACK5* was used as the starting point for a rigid-body refinement where the whole molecule was treated as one planar rigid body ($B=4\cdot0$ Å^2) with distances and angles taken from related structures. The $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ was $0\cdot186$ after refinement at this point. Significantly, the molecular position derived from *PACK5* did not change much on structure-factor least-squares refinement. The fractional changes in the molecular center were $|\Delta x| = 0\cdot02$, $|\Delta y| = 0\cdot00$, and $|\Delta z| = 0\cdot02$; the changes in the three angles used to describe the molecular rotations were $|\Delta\varphi| = 1\cdot9°$, $|\Delta\theta| = 5\cdot7°$, and $|\Delta\varrho| = 0\cdot5°$. At this point the molecule was split between the hydrazone nitrogens and refined as two rigid groups giving $0\cdot153$

Table 2 (cont.)

	x	y	z	B(Å^2)
H(1)	382 (5)	219 (11)	587 (5)	6·3 (26)
H(2)	288 (3)	131 (6)	259 (3)	0·6 (13)
H(3)	416 (3)	190 (6)	370 (3)	1·0
H(6)	69 (4)	66 (7)	430 (3)	2·1 (13)
H(9)	638 (3)	285 (7)	419 (3)	1·0
H(10)	800 (4)	323 (7)	360 (4)	1·8 (15)
H(11)	940 (5)	399 (8)	471 (3)	2·8 (15)
H(12)	909 (4)	428 (7)	615 (3)	2·7 (13)
H(14)	788 (4)	397 (6)	720 (3)	0·2 (14)
H(15)	625 (5)	393 (9)	777 (4)	4·5 (22)

for R and $0\cdot225$ for $R_w\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$. We proceeded directly to a refinement with anisotropic temperature factors for all non-hydrogen atoms giving $0\cdot076$ for R and $0\cdot097$ for R_w [$F>2\sigma(F)$ reflections used here]. All the hydrogen atoms bound to carbon atoms were found on an electron-density difference map and their positions and thermal parameters were refined. The hydrogen bound to N(1) was found on a general electron-density difference map calculated in the N(1), O(1), and O(2) plane; it was also included in the refinement.

The final refinements were carried out in two sections: (*a*) all the parameters (positional and thermal) associated with N(1) and the 2-nitro-4-chlorophenyl part of the molecule, and (*b*) all the parameters associated with N(2) and the 1,2-naphthoquinone part of the molecule. The isotropic temperature factors of H(3) and H(9) were fixed at $1\cdot0$ Å^2 in the final refinement, they tended to oscillate around zero. The final R values for 1018 reflections with $F>\sigma(F)$ were $0\cdot048$ for R and $0\cdot059$ R_w: the corresponding values for all the data (1117 reflections) are $0\cdot057$ for R and $0\cdot060$ for R_w. The standard deviation of an observation of unit weight is $1\cdot55$.

Table 2. Final coordinates and thermal parameters

Standard deviations are given in parentheses. The temperature factor has the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Non-hydrogen atom data are $\times 10^4$; hydrogen atom x,y, and z's are $\times 10^3$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	760 (1)	399 (2)	2577 (1)	65 (1)	452 (5)	43 (5)	−17 (2)	−7 (1)	−9 (2)
O(1)	4650 (3)	2859 (6)	6887 (2)	59 (3)	460 (13)	33 (2)	−8 (5)	14 (2)	−6 (4)
O(2)	2467 (3)	1583 (5)	6319 (2)	58 (3)	374 (12)	37 (2)	−7 (4)	1 (2)	−4 (4)
O(3)	895 (3)	1302 (6)	5791 (2)	46 (3)	541 (15)	61 (2)	−20 (5)	19 (2)	−42 (4)
N(1)	3977 (3)	2130 (6)	5338 (3)	41 (4)	211 (12)	39 (3)	0 (5)	6 (3)	9 (4)
N(2)	4934 (3)	2490 (5)	5115 (2)	44 (3)	164 (9)	32 (2)	3 (4)	5 (2)	6 (4)
N(3)	1821 (3)	1435 (5)	5713 (3)	47 (4)	237 (12)	39 (3)	2 (5)	11 (3)	−14 (4)
C(1)	1693 (4)	951 (6)	3389 (3)	54 (4)	186 (13)	38 (3)	17 (6)	−11 (3)	3 (5)
C(2)	2729 (4)	1257 (7)	3198 (4)	56 (4)	202 (15)	33 (3)	2 (6)	10 (3)	11 (5)
C(3)	3460 (4)	1632 (7)	3848 (3)	43 (4)	182 (14)	39 (3)	0 (6)	−3 (3)	3 (5)
C(4)	3208 (4)	1735 (6)	4695 (3)	49 (4)	128 (12)	31 (3)	−7 (5)	4 (3)	−4 (4)
C(5)	2171 (4)	1399 (6)	4860 (3)	43 (4)	161 (13)	28 (3)	5 (5)	14 (3)	10 (4)
C(6)	1417 (4)	1020 (7)	4215 (3)	52 (5)	189 (14)	37 (3)	7 (6)	−3 (3)	−9 (5)
C(7)	5676 (4)	2945 (6)	5693 (3)	45 (4)	182 (14)	29 (3)	−1 (5)	−4 (3)	0 (5)
C(8)	6701 (4)	3251 (6)	5403 (3)	34 (4)	138 (12)	37 (3)	−10 (5)	5 (3)	1 (5)
C(9)	6884 (4)	3146 (7)	4543 (4)	59 (5)	201 (15)	38 (4)	−9 (6)	4 (3)	−6 (5)
C(10)	7864 (4)	3385 (7)	4262 (4)	66 (5)	221 (15)	40 (3)	−8 (6)	20 (4)	−4 (5)
C(11)	8695 (5)	3707 (7)	4862 (4)	51 (5)	205 (15)	63 (4)	−15 (6)	−1 (4)	−3 (6)
C(12)	8537 (4)	3858 (7)	5707 (4)	64 (5)	181 (14)	45 (4)	−13 (6)	−4 (4)	−10 (6)
C(13)	7534 (4)	3625 (6)	5985 (3)	44 (4)	166 (13)	32 (3)	−6 (5)	4 (3)	0 (5)
C(14)	7334 (5)	3832 (7)	6869 (4)	57 (5)	209 (15)	40 (4)	−6 (7)	−8 (4)	13 (5)
C(15)	6413 (5)	3634 (7)	7179 (4)	57 (5)	236 (15)	42 (3)	−5 (6)	2 (4)	−9 (6)
C(16)	5515 (4)	3130 (7)	6607 (3)	59 (5)	209 (15)	45 (3)	5 (6)	1 (4)	5 (5)

Table 3. *Observed and calculated structure factors*

The table contains running index h, $5F_o$, $5F_c$ and an asterisk to indicate an unobserved reflection.

Scattering factors for the neutral atoms were used (Hanson, Herman, Lea & Skillman, 1964). The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement. The final parameters are given in Table 2. The observed and calculated structure factors are listed in Table 3.

Discussion

An *ORTEP* (Johnson, 1965) plot of the molecule illustrating the atom numbering used here is shown in Fig. 1. For clarity in this figure the hydrogen atoms were all plotted with 2·0 Å² temperature factors. The molecule has no special point symmetry although it is not far from C_s (m). The data for the least-squares plane through the whole molecule as well as for other portions of the molecule are given in Table 4. The whole molecule is essentially planar except for the NO_2 group which is tilted out of the plane by 7·8°. Individual interatomic distances and angles are given in Table 5.
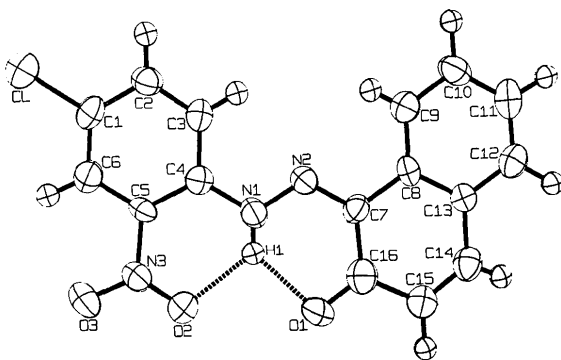

Fig. 1. Molecular structure of 1,2-naphthoquinone 1-(2-nitro-4-chloro-phenylhydrazone) (hydrogen atoms plotted with isotropic B's of 2·0 Å²).
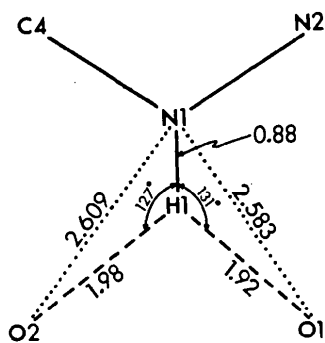

Fig. 2. Geometry of the bifurcated hydrogen bond.

Table 4. *Least-squares planes data*

Atomic deviations from plane (Å) .
Atoms with asterisks were not used in the plane calculation.

	1	2	3
Cl	0·019	−0·019	
O(1)	0·003		
O(2)	−0·237*		
O(3)	0·044*		
N(1)	−0·062	−0·006	
N(2)	−0·011		−0·042
N(3)	−0·076*		
C(1)	0·027	0·017	
C(2)	0·017	0·008	
C(3)	−0·018	−0·005	
C(4)	−0·033	0·001	
C(5)	−0·039	−0·006	
C(6)	−0·001	0·009	
C(7)	0·018		−0·002
C(8)	0·027		0·018
C(9)	0·060		0·051
C(10)	0·034		0·035
C(11)	−0·053		−0·040
C(12)	−0·058		−0·044
C(13)	−0·021		−0·018
C(14)	0·016		0·019
C(15)	0·051		0·044
C(16)	0·025		0·006

Equations of planes (a, b, c^*)

$$1 \quad -0\cdot1874X + 0\cdot9745Y - 0\cdot1236Z + 3\cdot762 = 0$$
$$2 \quad -0\cdot1834X + 0\cdot9773Y - 0\cdot1064Z + 2\cdot655 = 0$$
$$3 \quad -0\cdot1786X + 0\cdot9764Y - 0\cdot1212Z + 2\cdot713 = 0$$

Dihedral angles (°)

|			
Plane 1 ⎰ Plane 2 ⎱	1·0	N(3), O(2), O(3) ⎰ Plane 1 ⎱	7·8
Plane 1 ⎰ Plane 3 ⎱	0·5	N(3), O(2), O(3) ⎰ Plane 2 ⎱	7·0
Plane 2 ⎰ Plane 3 ⎱	0·9	C(1)–C(6) ⎰ C(7)–C(16) ⎱	1·1

Table 5. *Interatomic distances and angles*

Errors for the mean distances and angles estimated according to $[\sum(d_i - \bar{d})^2/n(n-1)]^{1/2}$.

Distances (Å)

Cl——C(1)	1·736 (6)	C(1)—C(2)	1·410 (7)	
N(1)—N(2)	1·333 (6)	C(2)—C(3)	1·368 (8)	
N(1)—C(4)	1·394 (7)	C(3)—C(4)	1·400 (8)	
N(2)—C(7)	1·312 (6)	C(4)—C(5)	1·404 (7)	
N(3)—C(5)	1·452 (7)	C(5)—C(6)	1·382 (8)	
N(3)—O(2)	1·226 (5)	C(6)—C(1)	1·377 (8)	
N(3)—O(3)	1·215 (6)	C(7)—C(8)	1·450 (7)	
C(16)-O(1)	1·248 (7)	C(8)—C(9)	1·395 (8)	
N(1)—H(1)	0·88 (8)	C(8)—C(13)	1·387 (7)	
		C(9)—C(10)	1·383 (8)	
C(2)—H(2)	0·99 (5)	C(10)—C(11)	1·396 (9)	
C(3)—H(3)	0·96 (4)	C(11)—C(12)	1·368 (9)	
C(6)—H(6)	1·00 (5)	C(12)—C(13)	1·408 (8)	
C(9)—H(9)	0·86 (4)	C(13)—C(14)	1·444 (8)	
C(10)-H(10)	1·07 (6)	C(14)—C(15)	1·328 (9)	
C(11)-H(11)	0·99 (6)	C(15)—C(16)	1·459 (8)	
C(12)-H(12)	1·01 (5)	C(17)-C(7)	1·477 (7)	
C(14)-H(14)	0·84 (5)		$\overline{1·402\ (9)}$	
C(15)-H(15)	0·99 (7)			
	$\overline{0·97\ (2)}$	H(1)···O(1)	1·92 (7)	
		H(1)···O(2)	1·98 (7)	

Angles (°)

C(4)—N(1)—N(2)	118·1 (4)	Cl——C(1)—C(2)	119·5 (4)	
N(1)—N(2)—C(7)	120·4 (4)	Cl——C(1)—C(6)	119·5 (4)	
C(5)—N(3)—O(2)	118·9 (4)	C(3)—C(4)—N(1)	120·0 (4)	
C(5)—N(3)—O(3)	117·9 (4)	C(5)—C(4)—N(1)	122·4 (4)	
C(2)—N(3)—O(3)	123·1 (4)	N(2)—C(7)—C(8)	116·9 (4)	
		N(2)—C(7)—C(16)	123·5 (4)	
C(1)—C(2)—C(3)	118·8 (5)	C(7)—C(16)-O(1)	121·8 (4)	
C(2)—C(3)—C(4)	121·9 (5)	C(15)-C(16)-O(1)	120·6 (5)	
C(3)—C(4)—C(5)	117·5 (4)			
C(4)—C(5)—C(6)	121·7 (4)	H(2)—C(2)—C(1)	118 (3)	
C(5)—C(6)—C(1)	119·1 (5)	H(2)—C(2)—C(3)	123 (3)	
C(6)—C(1)—C(2)	121·0 (5)	H(3)—C(3)—C(2)	117 (3)	
C(7)—C(8)—C(9)	121·6 (4)	H(3)—C(3)—C(4)	121 (3)	
C(7)—C(8)—C(13)	120·0 (4)	H(6)—C(6)—C(5)	125 (3)	
C(9)—C(8)—C(13)	118·4 (4)	H(6)—C(6)—C(1)	116 (3)	
C(8)—C(9)—C(10)	122·1 (5)	H(9)—C(9)—C(8)	119 (3)	
C(9)—C(10)-C(11)	118·6 (5)	H(9)—C(9)—C(10)	119 (3)	
C(10)-C(11)-C(12)	120·7 (6)	H(10)-C(10)-C(9)	121 (3)	
C(11)-C(12)-C(13)	120·2 (5)	H(10)-C(10)-C(11)	120 (3)	
C(12)-C(13)-C(8)	120·1 (4)	H(11)-C(11)-C(10)	123 (3)	
C(12)-C(13)-C(14)	121·6 (5)	H(11)-C(11)-C(12)	116 (3)	
C(8)—C(13)-C(14)	118·2 (4)	H(12)-C(12)-C(11)	123 (3)	
C(13)-C(14)-C(15)	125·1 (6)	H(12)-C(12)-C(13)	116 (3)	
C(14)-C(15)-C(16)	119·3 (5)	H(14)-C(14)-C(13)	114 (3)	
C(15)-C(16)-C(7)	117·6 (5)	H(14)-C(14)-C(15)	121 (3)	
C(16)-C(7)—C(8)	119·6 (4)	H(15)-C(15)-C(14)	126 (4)	
	$\overline{120·2\ (4)}$	H(15)-C(15)-C(16)	114 (4)	
			$\overline{120\ (1)}$	
N(1)—H(1)···O(1)	131 (6)			
N(1)—H(1)···O(2)	127 (6)			
	$\overline{129\ (2)}$			

An important feature of this structure is the determination of the tautomeric conformation and, a related point, the nature of the intramolecular hydrogen bonding. This point was established by the explicit location of H(1). The H(1) position was determined (0·4 e Å³) from an electron-density difference map calculated in the N(1), O(1), and O(2) plane with all atom contributions except H(1) subtracted out of the model. This alone is sufficient to establish the

hydrazone (Ia) as the predominant tautomer in the solid state. This sets up a bifurcated hydrogen-bonding situation involving N(1)–H(1) with O(1) and O(2). The details of this geometry are shown in Fig. 2. The resulting distances and angles involved in the bifurcated hydrogen bond are in the range found for nitrogen donors and oxygen acceptors (Hamilton & Ibers, 1968). Examples of bifurcated hydrogen bonds in organic molecules are discussed in some detail by Donohue (1968). There is some evidence for a stronger hydrogen bond to O(1) (shorter H···O distance, larger N–H···O angle, and greater planarity), but the H(1)··· O(1), O(2) environment is symmetric within experimental error.

The Cl–C as well as the C–N and N–O distances in the NO₂ group are similar to those observed in other benzene-substituted organic compounds (Kennard *et al.*, 1972). Likewise the benzene C–C and C–H distances are like those usually found in related compounds. The hydrazone portion of the molecule is of special interest.
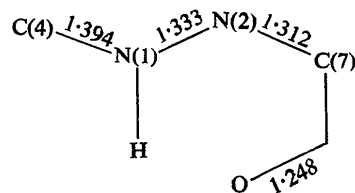
The geometry here as it pertains to the hydrazone-azo question has been discussed in detail by Pendergrass, Paul & Curtin (1972); they list literature values of bond lengths to be expected for the two tautomers.

N–N	1·33–1·38 Å	N=C	1·27–1·29 Å
N=N	1·23–1·28	N–C(amide)	1·30–1·41

The important point is that our distances fit into the pattern for the hydrazone tautomer (Ia). Our N–N is on the low end of the range quoted and our N=C is slightly larger than observed in some related compounds suggesting perhaps that there might be some small contribution present from the azo tautomer.
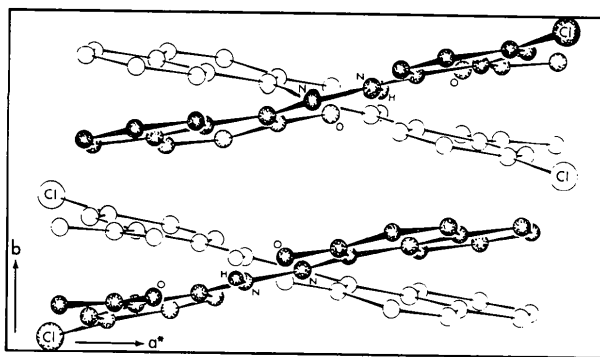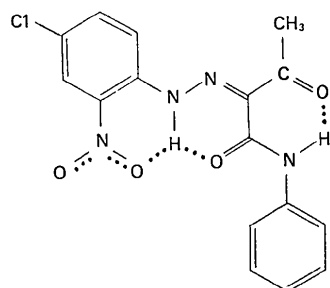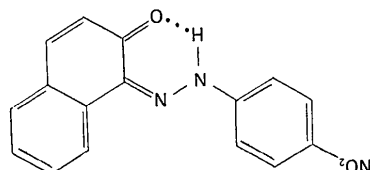

Fig. 3. The crystal packing viewed along c (hydrogen atoms have been omitted).

However, on the whole we feel that any azo contribution to the valence-bond structure is very small and probably nonexistent for the solid state.
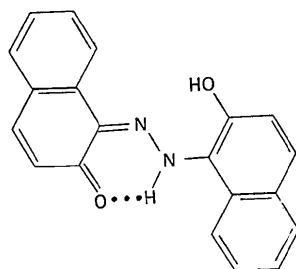
The following three compounds are of particular interest for comparison with the structure reported here.
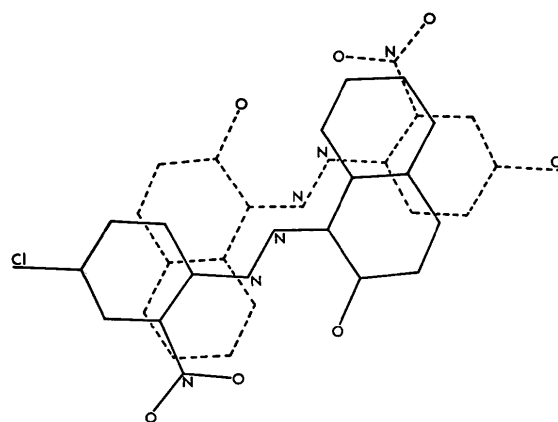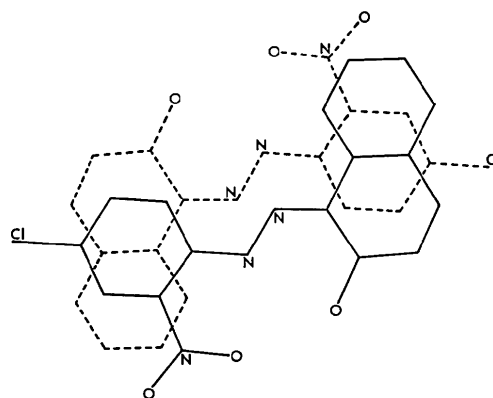

(II)

(III)

(IV)

(a)

(b)

Fig. 4. (a) Overlap between molecules at x,y,z, and $1-x$, $-y,1-z$; the perpendicular distance between parallel molecules is 3·40 Å. (b) Overlap between molecules at x,y,z, and $1-x,1-y,1-z$; the perpendicular distance between parallel molecules is 3·39 Å.

Compound	C(sp^2)-N	N-N	N=C	C=O
(Ia)	1·394 (7) Å	1·333 (6) Å	1·312 (6) Å	1·248 (7) Å
(II)	1·36	1·33	1·27	1·21
(III)	1·410	1·345 (7)	1·331 (10)	1·259 (10)
(IV)		1·319 (7)		

The remaining distances in (IV) (Cherin, 1973) are not given since they are affected in the refinement by crystallographic disorder. The authors reporting the structures of (II) (Mez, 1968) and (III) (Grainger & McConnell, 1969) use the azo name but they are best described as hydrazones, as noted also by Pendergrass, Paul, & Curtin (1972). The four structures have two common and important features: (a) they are primarily hydrazones in the solid state and (b) they are all essentially planar owing in part at least to intramolecular hydrogen bonding. An intriguing question is whether any of the so called 'azo' pigments with vicinal hydroxy groups are really azo compounds.

All intermolecular contacts were examined. The shortest contacts were 3·319 Å between nonhydrogen atoms [C(2)-O(2)], 2·453 Å between nonhydrogen and hydrogen atoms [O(3)-H(6)], and 2·236 Å between hydrogen atoms [H(11)-H(11)] at $2·0-x,1·0-y,1·0-z$]. The crystal packing in one unit cell is shown in Fig. 3. We looked in detail at the stacking for unusual intermolecular interactions between parallel molecules. The molecular overlap viewed normal to the molecular planes is shown in Fig. 4 for the overlap between a given molecule and its neighbors in both directions. The perpendicular distance between molecules in Fig. 4(a) is 3·39 Å while it is 3·40 Å in Fig. 4(b). The overlap

exemplified in Fig. 4(a) is distinctly better than in Fig. 4(b) with respect to the usual charge-transfer type of overlap (Prout & Kamenar, 1973); however, the distance between molecules is only 0·01 Å shorter in Fig. 4(a) than in Fig. 4(b). Although the overlap in Fig. 4(a) is reminiscent of that found in $\pi-\pi^*$ molecular complexes we feel that the magnitude of the distance between parallel molecules and the similarity of this distance for the two types of overlap is evidence that this merely reflects the most efficient packing of parallel molecules without any formal charge-transfer interactions.

References

CHERIN, P. (1973). Amer. Cryst. Assoc. Summer Meeting, Univ. of Connecticut, Storrs, Connecticut, Abstract G2, p. 149.

DONOHUE, J. (1968). Structural Chemistry and Molecular Biology, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco: Freeman.

GRAINGER, C. T. & McCONNELL, J. F. (1969). Acta Cryst. B25, 1962–1970.

GUGGENBERGER, L. J. (1968). Inorg. Chem. 7, 2260–2264.

HAMILTON, W. C. & IBERS, J. A. (1968). Hydrogen Bonding in Solids, p. 262. New York: Benjamin.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). Acta Cryst. 17, 1040–1044.

JOHNSON, C. K. (1965). ORTEP. Oak Ridge National Laboratory Report ORNL-3794.

KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSON, R. C. & TOWN, W. G. (1972). Molecular Structures and Dimensions, Vol. A1. Utrecht: Oosthoek.

KUDER, J. E. (1972). Tetrahedron, 28, 1973–1981.

MEZ, H. C. (1968). Ber. Bunsenges. Phys. Chem. 72, 389–392.

PENDERGRASS, D. B. JR, PAUL, I. C. & CURTIN, D. Y. (1972). J. Amer. Chem. Soc. 94, 8730–8737.

PROUT, C. K. & KAMENAR, B. (1973). Molecular Complexes, Vol. 1, edited by R. FOSTER, pp. 151–207. New York: Crane & Russak.

WILLIAMS, D. E. (1964). PACK2, a Fortran Crystallographic Molecular Packing Program, USAEC Report IS-1042. PACK5 is a later-version packing program (private communication).

WILLIAMS, D. E. (1969). Acta Cryst. A25, 464–470.

The Crystal and Molecular Structure of 3β-Hydroxy-20-oxo-5-pregnene-16α-carbonitrile

BY A. TERZIS

Chemistry Department, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

AND T. THEOPHANIDES

Chemistry Department, University of Montreal, Montreal, Quebec H3C 3V1, Canada

The synthetic steroid 3β-hydroxy-20-oxo-5-pregnene-16α-carbonitrile, $C_{22}H_{31}O_2N$, is a potent inducer of liver microsomal enzymes. The structure was determined from room-temperature counter-collected data by the application of direct methods. The space group is $P2_1$ with cell dimensions $a = 12\cdot204$ (2), $b = 6\cdot300$ (1), $c = 12\cdot273$ (2) Å and $\beta = 95\cdot47$ (2)°; $D_m = 1\cdot20$, $D_x = 1\cdot207$ g cm^{-3} for $Z = 2$. 1825 intensities were measured. The structure was refined by conventional least-squares techniques to an R index of 3·0%. The structure packs in antiparallel chains held together by van der Waals forces. There is one OH···O hydrogen bond of 2·883 Å within the chains.

Introduction

From extensive studies of the effect of steroids on body resistance (Selye, 1970, 1971) it has become evident that in addition to the two previously explored protective mechanisms (nervous and immunologic) there exists a third defense system with which the organism can respond, the steroidal one. In this respect the steroids are generally classified as: (a) syntoxic, if they protect against a pathogen by increasing the tolerance towards it, by suppressing non-specific inflammatory reactions against it (glucocorticoids) and (b) catatoxic, if they actually destroy the aggressor through the induction of hepatic microsomal or other enzymes.

Some catatoxic steroids are also endowed with classic hormonal activities, but the catatoxic effect does not depend on any other known pharmacological action; indeed, the synthetic steroid pregnenolone-16α-carbonitrile (PCN: Fig. 1), a very potent catatoxic steroid, is devoid of any other steroidal activity or toxic property.

We undertook the X-ray analyses of some of these