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The Crystal Structure of the Diacetate of Naphthazarin

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The X-ray analysis of $C_{14}H_{10}O_6$ has been carried out with three-dimensional diffractometer data and refined to an R index of 0·068 for 728 observed reflexions. The compound crystallizes in the space group $C2/c$, with $a = 12{\cdot}400\,(6)$, $b = 11{\cdot}208\,(2)$, $c = 11{\cdot}077\,(3)$ Å, $\beta = 123{\cdot}87\,(4)^\circ$ and $Z = 4$. The two rings of the compound have different characters: one is quinonoid while the other has a benzenoid form, the common bond being 1·418 (5) Å long. There exists an intramolecular interaction between the acetyl group and the quinonoid oxygen, with a C · · · O contact of 2·748 (6) Å.

Introduction

Several studies have been made of the structure of naphthazarin: (*a*) In solution (Schmand & Boldt, 1975) it seems to exist as 5,8-dihydroxy-1,4-naphthoquinone. (*b*) X-ray data (Pascard-Billy, 1962; Cradwick & Hall, 1971), however, indicate the *ana*-quinonoid* structure 4,8-dihydroxy-1,5-naphthoquinone. The diacetate of naphthazarin has been studied in solution by NMR techniques (Brockmann & Zeek, 1968) and shown to exist as 5,8-diacetoxy-1,4-naphthoquinone, the *ana*-quinonoid form being excluded. However, other work (Fariña, Lora-Tamayo & Suarez, 1963; Alvarado, Fariña & Martin, 1970) on naphthazarin diacetates and their substituted derivatives shows that a trans-acylation process is possible under some 'soft' conditions. This means that the quinonoid and the aromatic characters of the two rings could be interchangeable.

From the X-ray results for naphthazarin and despite the *ana*-quinonoid form being much less stable (Schmand & Bolt, 1975), it is possible that in the solid state naphthazarin diacetate exists as 4,8-diacetoxy-1,5-naphthoquinone, which may be formed in the first stage of the transacylation process. In order to verify this and to determine the orientation of the acetyl groups, we have undertaken the crystallographic study of the title compound.

Experimental

Suitable dark-yellow crystals were kindly supplied by Professor F. Fariña. The crystal data are given in Table 1. A prismatic crystal of approximate dimensions 0·08 × 0·06 × 0·06 mm was used on a Philips PW 1100 automatic diffractometer with graphite monochromator and Mo $K\alpha$ radiation. 1666 independent reflexions were collected up to 30° in θ, with the $\omega/2\theta$ scan mode. Of these, 728 were considered observed by the $2\sigma(I)$ criterion, σ being determined from counting statistics.

Table 1. *Crystal data*

Standard deviations, given in parentheses, refer to the least significant digits.

Molecular formula	$C_{14}H_{10}O_6$
M_r	274·24
Crystal system	Monoclinic
Space group	$C2/c$
Wavelength (Mo $K\bar{\alpha}$)	0·7107 Å
a	12·400 (6) Å
b	11·208 (2)
c	11·077 (3)
β	123·87 (4)°
Z	4
V	1278·23 Å^3
D_{obs}(flotation)	1·06 g cm^{-3}
D_{cal}	1·062
$F(000)$	568
μ	0·91 cm^{-1}

Structure determination and refinement

The data were corrected for the Lorentz–polarization factor, but not for absorption due to the low value of μ. The structure was solved by direct methods (*MULTAN*: Main, Woolfson, Lessinger, Germain &

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* See Zahn (1934) for the definition of '*ana*'.

Declercq, 1974) and refined by least-squares techniques. The H atoms were located on a difference Fourier map. The refinement was continued with a mixed thermal model, with all the H atoms isotropic. The $\langle w\Delta^2 \rangle$ values ($\Delta = |F_o| - |F_c|$) were examined as a function of $|F_o|$ and $\sin\theta/\lambda$. The plots suggested the following weighting scheme: $\sqrt{w} = 1/\sigma_f\sigma_s$ with $\sigma_f = a + b|F_o|$ and $\sigma_s^2 = c + d\sin\theta/\lambda$ where the coefficients (Table 2) depend upon the range of the variables. After least-squares refinement with this scheme the final weighted $[R_w = (\Sigma\, w\Delta^2/\Sigma\, w|F_o|^2)^{1/2}]$ and unweighted agreement indices were 0·071 and 0·068 respectively for the 728 observed reflexions and 111 refinement parameters. A final difference synthesis showed no significant peaks, the background being in the range $\pm 0{\cdot}37$ e Å^{-3}. No trends were noticed in the final $\langle w\Delta^2 \rangle$ analysis.

The final values of the positional and thermal parameters are given in Table 3. The atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).*

Results and discussion

Figs. 1 and 2 show only the bond distances and angles within half the molecule since it is situated on a crystallographic twofold axis.

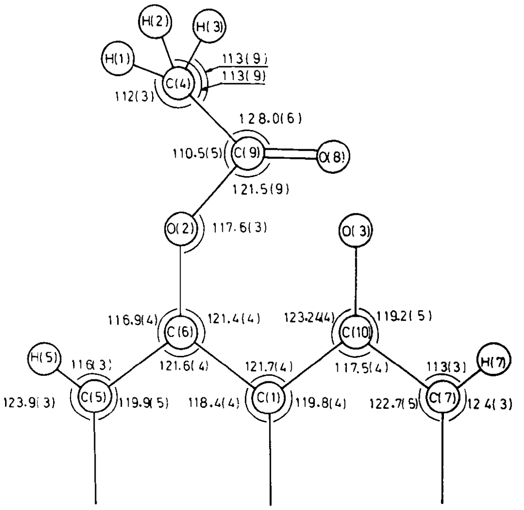

Fig. 1. Bond distances.

Table 2. *Coefficients for the weighting scheme*

	a	b		c	d
$0 \le \lvert F_o\rvert < 4{\cdot}2$	1·538	0·135	$0 \le \sin\theta/\lambda < 0{\cdot}51$	1	−0·345
$4{\cdot}2 \le \lvert F_o\rvert < 12{\cdot}0$	2·944	−0·172	$0{\cdot}51 \le \sin\theta/\lambda \le 0{\cdot}68$	−1·262	3·927
$12{\cdot}0 \le \lvert F_o\rvert \le 300$	0·615	0·033			

Table 3. *Final atomic coordinates and thermal parameters* [*thermal parameters given according to the expression* $\exp(-2\pi^2\Sigma U_{ij}a^*_ia^*_jh_ih_j)$]

The least-squares e.s.d.'s given in parentheses affect the last digits.

	x	y	z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
C(1)	0·5383 (3)	0·7903 (4)	0·8270 (4)	36 (2)	49 (2)	55 (2)	0 (2)	31 (2)	0 (3)
O(2)	0·6598 (3)	0·6746 (3)	1·0492 (3)	42 (2)	80 (3)	62 (2)	11 (1)	31 (2)	17 (2)
O(3)	0·6366 (3)	0·9118 (3)	1·0391 (4)	74 (2)	74 (2)	55 (2)	−11 (2)	36 (2)	−8 (2)
C(4)	0·7114 (6)	0·6962 (9)	1·2853 (6)	63 (3)	122 (6)	62 (3)	12 (4)	36 (3)	26 (4)
C(5)	0·5387 (5)	0·5755 (5)	0·8248 (6)	53 (3)	48 (3)	84 (3)	5 (3)	37 (3)	11 (3)
C(6)	0·5760 (4)	0·6811 (4)	0·8990 (5)	37 (2)	54 (4)	60 (3)	6 (2)	29 (2)	9 (2)
C(7)	0·5352 (5)	1·0154 (5)	0·8214 (6)	97 (4)	52 (3)	74 (3)	−7 (3)	58 (3)	−7 (3)
O(8)	0·4943 (3)	0·7023 (3)	1·0740 (3)	45 (2)	92 (2)	76 (2)	7 (2)	39 (2)	16 (2)
C(9)	0·6083 (4)	0·6927 (4)	1·1299 (5)	51 (2)	65 (3)	68 (3)	6 (3)	38 (2)	20 (3)
C(10)	0·5765 (4)	0·9053 (4)	0·9075 (6)	52 (2)	52 (3)	63 (3)	−3 (2)	40 (2)	−2 (3)

	x	y	z	10^3U		x	y	z	10^3U
H(1)	0·6780 (54)	0·7003 (56)	1·3428 (62)	65 (19)	H(5)	0·5705 (41)	0·5063 (51)	0·8814 (47)	36 (15)
H(2)	0·7690 (86)	0·7645 (78)	1·3126 (81)	123 (35)	H(7)	0·5685 (49)	1·0817 (51)	0·8764 (53)	49 (17)
H(3)	0·7561 (60)	0·6316 (58)	1·3156 (67)	60 (23)					

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32069 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The molecule consists of a quinonoid ring and an aromatic ring, namely C(1)—C(10)—C(7) and C(1)—C(6)—C(5) together with their symmetry-related atoms.

Both rings are planar within the estimated errors, with maximum deviations of ±0·01 Å, but the molecule is non-planar, the angle between the two ring planes being 1·6°; this angle increases to 8·0° when the planes C(1)—C(6)—O(2) and C(1)—C(10)—O(3) are considered.

Following from this it is noticeable that O(3) is −0·06 Å from the quinone plane, while O(2) is 0·09 Å (*i.e.* in the opposite direction) from the aromatic ring. Moreover the angles O(3)—C(10)—C(1) and O(2)—C(6)—C(5), 123·2 (4) and 116·9 (4)° respectively, illustrate the deviation of both O atoms from the rings.

Of the distances in the rings it is worth remarking that C(10)—C(1), C(10)—C(7) and C(5)—C(6) are a little shorter than the expected values. Only the common bond has a distance longer than that expected for the quinonoid form.

The acetate group is planar, with a maximum deviation of 0·004 Å for C(9). Its angle with the aromatic ring is 82·3°. This group is almost perpendicular to the ring but twisted towards the quinonoid O through torsion around C(6)—O(2) and O(2)—C(9) of 6·6 and 78·2° respectively. The distances O(8)···C(1) = 3·227, O(8)···C(5) = 3·411 (8) Å show that O(8) is situated towards C(1).

The intramolecular distances O(2)···C(1) = 2·424 (5), O(2)···C(5) = 2·347 (6), O(3)···C(1) = 2·381 (5) and O(3)···C(7) = 2·317 (6) Å show that O(2) is directed towards C(5) and O(3) towards C(7). The distances C(6)···C(10) = 2·515 (7) Å *versus* O(2)···O(3) = 2·669 (5) Å indicate that the C—O bonds are not parallel. In addition, O(2)···O(3) and O(3)···C(9) [= 2·748 (6) Å] are short for normal contacts between the atoms. These cause the deviations from the planes mentioned above, to different sides of the rings, and the opening of the angles at C(6) and C(10).

In spite of this separation, the distance O(3)···C(9) remains short, although the effect of this shortening is only weak when the characteristics of the molecule are taken into account. However, its existence indicates the possible contribution of polar forms to the resonance in the molecule (Fig. 3), which could explain the variation in the bond distances.

Thus it seems possible that the O(2)—C(9) bond, under some circumstances, could weaken and so initialize a transacylation process through an *ana*-quinone form, with perturbation of the electronic equilibrium in the rings. The interchange of the acetyl group as well as character of the rings would restore the stability of the molecule.

Neither hydrogen bonds nor short hydrogen contacts have been detected (Fig. 4). The molecules pack together, through van der Waals forces, on the (4̄02) planes – the strongest in the diffraction pattern.

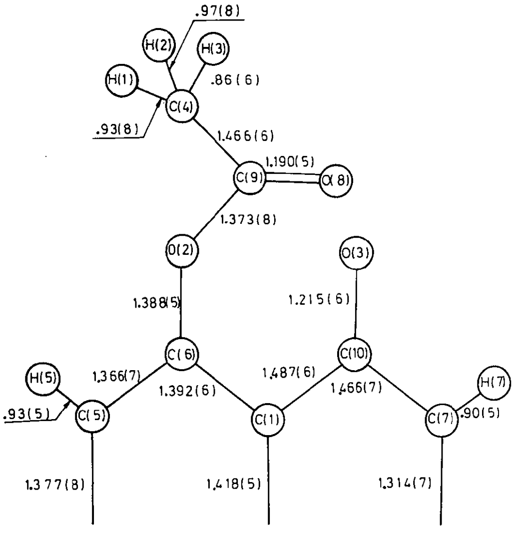

Fig. 2. Bond angles.

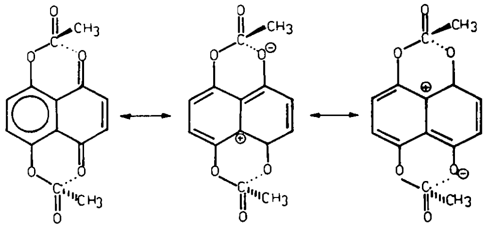

Fig. 3. Contributing resonance forms.

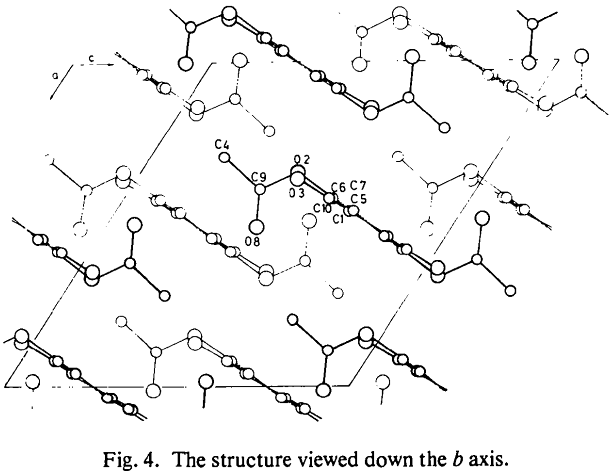

Fig. 4. The structure viewed down the *b* axis.

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The Crystal and Molecular Structure of BNA, a Cyclotetracondensate from Quaternary Salts of Nicotinamide

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Four molecules of quaternary salts of nicotinamide cyclocondense to form a new product (BNA). The crystals of the title compound ($C_{52}H_{48}N_8O_4$) are monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 14{\cdot}357$ (3), $b = 10{\cdot}736$ (1), $c = 34{\cdot}017$ (6) Å and $\beta = 123{\cdot}38$ (3)°. The structure has been determined by direct and Fourier methods and refined by least-squares analysis to an R value of 0·067 for 2472 observed reflexions. Four intramolecular hydrogen bonds involving the O atoms may explain the lipophilic properties of the molecule.

Introduction

A new reaction of quaternary salts of nicotinamide has been found and checked with more than 20 salts, differently substituted at the pyridinium N (Gündel, 1973; Gündel, Buecher & Hagedorn, 1974): four molecules of nicotinamide salts cyclize on addition of the equivalent amount of base. The cyclotetracondensate BNA, the formula of which is given in Fig. 1, results after elimination of hydrogen chloride from 1-benzyl-3-carbamoylpyridinium chloride.

The cyclocondensed products are lipophilic and can be split quantitatively by acids, such as hydrogen chloride, to the quaternary salts of nicotinamide. The possibility of transforming the hydrophilic salts of nicotinamide to a lipophilic form is of great interest.

As nicotinamide is part of the coenzyme NAD (nicotinamide adenine dinucleotide) it is suggested that NAD can cyclize in organisms in the same way.

To confirm the structure and conformation of the new cyclotetracondensate, BNA was submitted to an X-ray structure analysis.