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# Structures of Nitrogen-Containing Aromatic Compounds.
# IV. 1,4,5,8-Pyridazino[1,2-*a*]pyridazinetetrone

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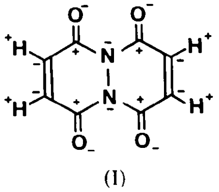
$C_8N_2O_4H_4$ (DIAZAN) is monoclinic, $P2_1/c$, $a$ = 13·805 (10), $b$ = 8·360 (5), $c$ = 21·500 (15) Å, $\beta$ = 107·3 (1)°, $V$ = 2369 Å$^3$, $D_m$ = 1·58 (1) g cm$^{-3}$, $Z$ = 12. $R$ = 0·054 for 3104 observed data (diffractometer, monochromated Mo $K\alpha$), all C, N and O atoms anisotropic, all H's included. Mean bond lengths (not corrected for thermal motion, ranges in parentheses): N–N 1·428 (5), N–C 1·418 (20), C–C 1·461 (15), C=C 1·317 (20), C=O 1·209 (10) Å. Although each N atom is trigonal $sp^2$-hybridized, the molecule is far from planar. The bond lengths show that DIAZAN is not aromatic although there is some electron delocalization in the O=C–N–C=O system. The structure is layered with the molecules lying in sheets at approximately $z = \frac{1}{12}, \frac{1}{4}$ and $\frac{5}{12}$. There are two types of short intermolecular C···O separations of 2·95 to 3·15 Å: (*a*) the O atom of a carbonyl group of a molecule in one layer is close to the C atom of a carbonyl group of a molecule in the adjacent layer; (*b*) the O atom of a carbonyl group of a molecule is in close contact with one H atom of another molecule within the same layer. A detailed description is given of the solution of the structure by direct methods.

## Introduction

The preparation and properties of 1,4,5,8-pyridazino[1,2-*a*]pyridazinetetrone were described by Kealy (1962). The analogous 1,4-dione was reported by Sasaki, Kanematsu & Ochiai (1972), and the crystal structure of the related compound 8b,8c-diazacyclopent[*fg*]acenaphthylene was reported by Atwood, Hrncir, Wong & Paudler (1974).

DIAZAN is readily formed by thermal decomposition of 3,6-pyridazinedione, and its reported melting point (247 °C) suggests not only stability of the molecule but unusually large intermolecular attractions in the solid. However, DIAZAN is rapidly hydrolysed in boiling water and Kealy (1962) concluded that it had 'a strained ring system', inferred from the position of the carbonyl stretching frequency in the infrared spectrum. Its UV–visible absorption spectrum is remarkably similar to that of 1,4-naphthaquinone (Sasaki *et al.*, 1972), suggesting aromatic character.

Consideration of electronegativities (Pauling, 1960) gives the charge distribution shown in (I), and a $\pi$-electron count suggests that the compound could be 'antiaromatic' (Lewis & Peters, 1975). Therefore, the crystal structure of DIAZAN has been determined to obtain accurate C–C, C–N and N–N bond lengths and thus an estimate of their bond orders and the degree of aromaticity of the compound.



(I)

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## Experimental

The compound was prepared according to the method of Kealy (1962). Suitable crystals were obtained by slow crystallization from acetone.

Cell dimensions (Table 1) were obtained by least-squares refinement of $2\theta$, $\chi$ and $\varphi$ angles for 25 reflexions measured on a Philips four-circle diffractometer. Intensities were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for $\theta$ between 3 and 25°. The $\omega/2\theta$ scan mode was used; the scan width was 1·0°, the scan time 25 s, and the background was counted for 25 s for each reflexion. Three reflexions were remeasured after every 60 reflexions; no crystal decomposition was detectable. Of the 4432 reflexions measured (including space-group extinctions), 3104 were classed as observed, *i.e.* $I > 1.65\sigma(I)$. Only Lorentz–polarization corrections were applied.

Table 1. *Crystal data*

| | |
|---|---|
| $C_8N_2O_4H_4$ | Monoclinic, $P2_1/c$ |
| $a = 13.805$ (10) Å | $V = 2369$ Å$^3$ |
| $b = 8.360$ (5) | $Z = 12$ |
| $c = 21.500$ (15) | $D_m = 1.58$ (1) g cm$^{-3}$ |
| $\beta = 107.3$ (1)° | $M_r = 192$ |

The structure (Fig. 1) was solved by a combination of Patterson and direct methods. A temperature-sharpened Patterson map showed that the structure was layered, with the molecules in sheets parallel to the $xy$ plane and separated by $z/6$ (about 3·5 Å). The dimensions of the molecule prevented it from lying at $z = 0$ and therefore it followed that the three independent molecules had to lie at $z = \frac{1}{12}, \frac{1}{4}$ and $\frac{5}{12}$ respectively. The orientation of the molecules in the $xy$ plane was deduced from the relative heights and distribution of the peaks about the origin: one side of the six-membered ring system lay parallel to $y$ while the O=C–C=O vectors made an angle of 60° with it. Severe overlap in the sections $W = 0, \frac{1}{6}, \frac{1}{3}$ and $\frac{1}{2}$ prevented a definite assignment of the $xy$ coordinates of the three molecules.

A Wilson plot and statistical analysis of the intensities confirmed the conclusions from the Patterson

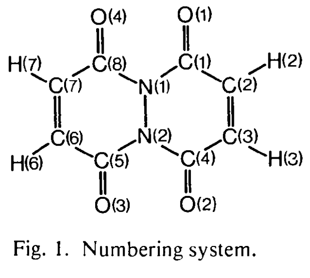

Fig. 1. Numbering system.

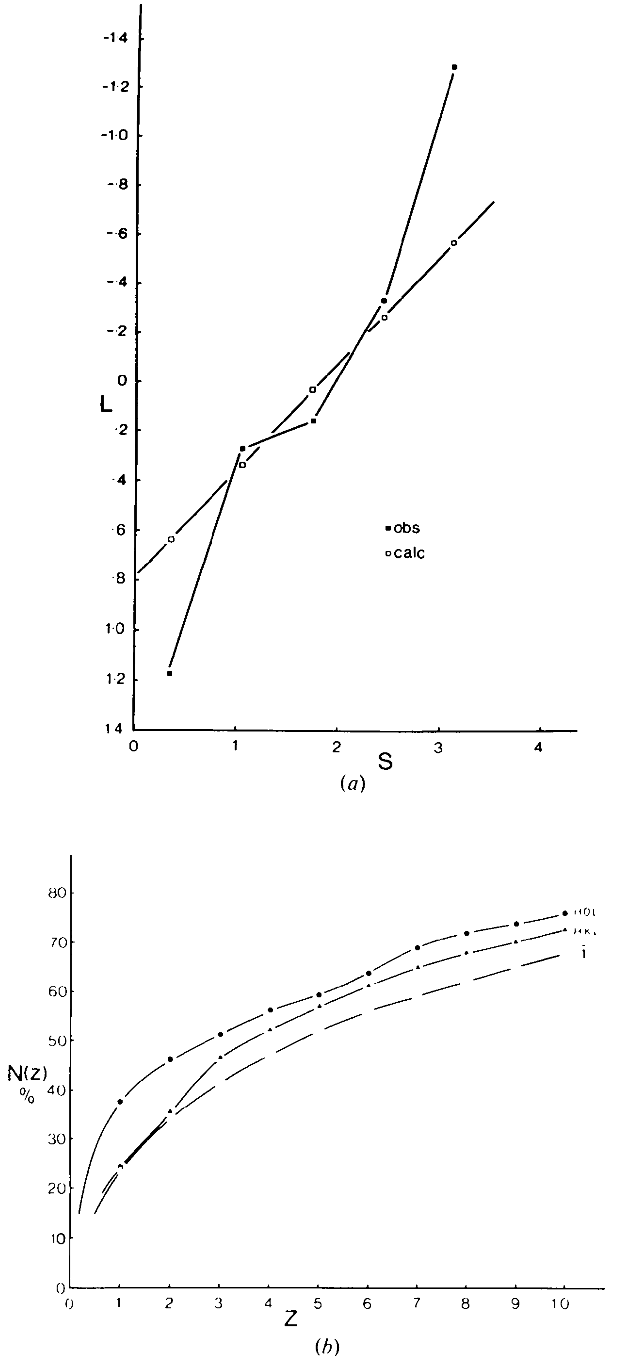

Fig. 2. (*a*) Wilson plot; $L = \ln(I/\Sigma f^2)$, $S = \sin^2\theta/\lambda^2$. The straight line is calculated to fit best the three middle points of the observed plot, and gives $B = 2.15$ Å$^2$, scale = 0·45. (*b*) Distribution of intensities: $N(Z)$ is the fraction of the reflexions with $I < Z\bar{I}$. The theoretical centric distribution is labelled $\bar{1}$. The curves for the $h0l$ and $hkl$ data (labelled HOL and HKL respectively) are typical of hypersymmetric distributions and are comparable with cases $n = 2$ and 3 in Table 1(*a*) while DIAZAN is equivalent to the molecule (*d*) in Fig. 8 of the paper by Rogers & Wilson (1953).

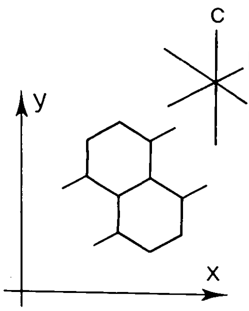

Fig. 3. Schematic representation of the orientation of the framework of DIAZAN relative to the $x$ and $y$ axes. The planes $a$, $b$ and $c$ are parallel to the sides of the six-membered rings and one of each class was included in the origin-definers and variables in program *SAYRE*. $a$: $h \sim k = 5$ to 8, $l$ small; $b$: $h \sim -k = 5$ to 8, $l$ small; $c$: $k \sim l$ small, $h \sim 12$. The molecular plane was defined by: $h \sim k$ small, $l \sim 10$ to 12 with a positive sign. Reflexions with $h \sim k$ small, $l \sim 6$ were expected to have a negative sign; *e.g.* 006, 016.

Table 2. *Reflexions used as the starting sets in program SAYRE*

(*a*) Origin definers with correct parities

| *h* | *k* | *l* | *E* | Starting set | Correct solution | Incorrect solution |
|---|---|---|---|---|---|---|
| 1 | 3 | 10 | 3·35 | + | + | + |
| −5 | 7 | 1 | 4·37 | + | + | + |
| 8 | 5 | 2 | 3·66 | + | + | + |
| 0 | 1 | 6 | 5·20 | − | − | − |
| 7 | 5 | 2 | 6·26 | − | − | − |
| 2 | 4 | 2 | 3·02 | + | − | − |
| 8 | 5 | 11 | 3·44 | + | + | + |
| −12 | 2 | 3 | 4·72 | + | + | + |
| 0 | 0 | 6 | 7·99 | | − | − |
| −7 | 5 | 8 | 5·52 | | + | + |
| −12 | 2 | 9 | 4·99 | | − | − |
| −5 | 3 | 1 | 4·29 | | − | − |
| −11 | 5 | 4 | 4·13 | | − | + |
| 1 | 1 | 4 | 4·05 | | − | − |

(*b*) Origin definers with incorrect parities*

| *h* | *k* | *l* | *E* | Starting set | Correct solution |
|---|---|---|---|---|---|
| 1 | 3 | 10 | 3·35 | + | + |
| 12 | 2 | 3 | 4·72 | + | + |
| −7 | 5 | 8 | 5·52 | + | + |
| 5 | 3 | 1 | 4·29 | − | − |
| 8 | 5 | 2 | 3·66 | + | + |
| 2 | 4 | 2 | 3·02 | + | − |
| 0 | 1 | 6 | 5·21 | − | − |
| −8 | 5 | 11 | 3·44 | + | + |
| 0 | 0 | 6 | 7·99 | | − |
| 7 | 5 | 2 | 6·26 | | − |
| −12 | 2 | 9 | 4·99 | | − |
| −5 | 7 | 1 | 4·37 | | + |
| −11 | 5 | 4 | 4·13 | | − |
| 1 | 1 | 4 | 4·05 | | − |

* When 852 was used in place of $\bar{7}58$ as an origin-definer, *SAYRE* was unable to generate the correct set of signs.

map (Fig. 2); *i.e.* the Wilson plot had a zigzag shape and the $h0l$ data showed that this projection was hypersymmetric (Kitaigorodskii, 1961; Rogers & Wilson, 1953). The distribution of $E$'s was also abnormal and very similar to that found by Sasvári (1975) for $C_6H_{11}$–$C_6H_{10}$–$C_6H_{11}$ ($\langle|E|\rangle = 0{\cdot}66$, $\langle|E^2|\rangle = 0{\cdot}84$, $\langle|E^2-1|\rangle = 1{\cdot}04$; $E$'s $> 3 = 0{\cdot}9\%$, $E$'s $> 2 = 3{\cdot}2\%$, $E$'s $> 1 = 16{\cdot}6\%$; the largest $E$ was 7·99 for 006). No attempt was made to rescale the $E$'s or to alter their values by choosing a different value for $B$.

The 380 $E$'s $> 1{\cdot}5$ were used to solve the structure with *SAYRE* (Long, 1965). The starting set was chosen by hand with the three origin-defining reflexions defined by planes parallel to two sides of the six-membered rings and the mean plane of the molecule (Fig. 3) (Laing, 1976). Five variables had to be used because, with only four, a large fraction of the $hkl$'s could not be reached by the $\Sigma_2$ calculations. The program was run with parameters NSORT = 1, NBACK = 1; and the correct solution had the highest consistency index (0·68) but required 14 cycles to converge and in the process the sign of one of the variables (242) changed. When this *correct* set of signs was used as the starting set, a different solution having a consistency index of 0·55 was obtained, also after 14 cycles (Table 2). The 12 largest $E$'s had the same signs as for the correct solution, but that of $\bar{1}\bar{1},5,4$ ($E = 4{\cdot}13$) was reversed and thereafter the pattern of signs was different.

The $E$ map from the correct solution revealed all 42 heavy atoms but some ghost peaks accompanied molecule $B$ ($z = \frac{1}{4}$). The coordinates derived from this map yielded $R = 0{\cdot}30$ and the structure was then refined by block-diagonal least squares, first isotropically ($R = 0{\cdot}16$) then anisotropically ($R = 0{\cdot}088$). The 12 H atoms were added and the parameters of the 42 heavy atoms refined to convergence: $R = 0{\cdot}054$ for 3104 observed data.* The scattering factors were those for neutral atoms, taken from *International Tables for X-ray Crystallography* (1962). Weights were proportional to $1/\sigma(F)$.

The atomic coordinates are given in Table 3, and the numbering system in Fig. 1. Bond lengths and angles are given in Table 4 and parameters describing various least-squares planes and deviations of the atoms from these planes are given in Table 5. The thermal ellipsoids of the C, N and O atoms are illustrated in Fig. 4.

The relatively large amplitudes of vibration of the atoms seemed to be at variance with the high melting point (Kealy, 1962), so a study was made of the thermal characteristics of DIAZAN. Crystals were heated on a Reichert-made Kofler hot-stage, open to the air,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32495 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional atomic coordinates* ($\times 10^4$ *for* N, C *and* O; $\times 10^3$ *for* H)

The estimated standard deviation in the last significant figure is shown in parentheses.

Molecule *A*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| N(1) | 3818 (1) | 5802 (2) | 878 (1) |
| N(2) | 4631 (1) | 6895 (2) | 923 (1) |
| O(1) | 2344 (1) | 5394 (2) | 1136 (1) |
| O(2) | 5020 (1) | 9479 (2) | 732 (1) |
| O(3) | 6361 (1) | 7182 (2) | 1191 (1) |
| O(4) | 3132 (1) | 3412 (2) | 443 (1) |
| C(1) | 2971 (2) | 6334 (3) | 1048 (1) |
| C(2) | 2866 (2) | 8060 (3) | 1117 (1) |
| C(3) | 3518 (2) | 9091 (3) | 1013 (1) |
| C(4) | 4437 (2) | 8578 (3) | 865 (1) |
| C(5) | 5624 (2) | 6300 (3) | 1028 (1) |
| C(6) | 5710 (2) | 4591 (3) | 905 (1) |
| C(7) | 4900 (2) | 3649 (3) | 703 (1) |
| C(8) | 3878 (2) | 4220 (3) | 645 (1) |
| H(2) | 229 | 848 | 126 |
| H(3) | 337 | 1026 | 102 |
| H(6) | 640 | 412 | 96 |
| H(7) | 499 | 251 | 58 |

Molecule *B*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| N(1) | 2205 (1) | 3908 (2) | 2538 (1) |
| N(2) | 2886 (1) | 2783 (2) | 2398 (1) |
| O(1) | 2010 (2) | 6373 (2) | 2946 (1) |
| O(2) | 4212 (1) | 2496 (2) | 1970 (1) |
| O(3) | 3416 (1) | 172 (2) | 2511 (1) |
| O(4) | 548 (2) | 4380 (3) | 2426 (1) |
| C(1) | 2552 (2) | 5464 (3) | 2767 (1) |
| C(2) | 3577 (2) | 5868 (3) | 2753 (1) |
| C(3) | 4131 (2) | 4912 (3) | 2507 (1) |
| C(4) | 3777 (2) | 3334 (3) | 2259 (1) |
| C(5) | 2738 (2) | 1120 (3) | 2477 (1) |
| C(6) | 1732 (2) | 649 (3) | 2492 (1) |
| C(7) | 1028 (2) | 1707 (4) | 2456 (2) |
| C(8) | 1210 (2) | 3414 (3) | 2463 (1) |
| H(2) | 388 | 693 | 294 |
| H(3) | 483 | 530 | 250 |
| H(6) | 157 | −52 | 252 |
| H(7) | 32 | 131 | 242 |

Molecule *C*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| N(1) | 431 (1) | 5780 (2) | 4167 (1) |
| N(2) | 1248 (1) | 6884 (2) | 4230 (1) |
| O(1) | −1044 (1) | 5378 (2) | 4424 (1) |
| O(2) | 1638 (1) | 9443 (2) | 3996 (1) |
| O(3) | 2966 (1) | 7245 (2) | 4587 (1) |
| O(4) | −155 (1) | 3246 (2) | 3874 (1) |
| C(1) | −441 (2) | 6310 (3) | 4323 (1) |
| C(2) | −599 (2) | 8032 (3) | 4306 (1) |
| C(3) | 37 (2) | 9047 (3) | 4174 (1) |
| C(4) | 1029 (2) | 8545 (3) | 4111 (1) |
| C(5) | 2266 (2) | 6320 (3) | 4404 (1) |
| C(6) | 2400 (2) | 4612 (3) | 4346 (1) |
| C(7) | 1625 (2) | 3608 (3) | 4163 (1) |
| C(8) | 568 (2) | 4132 (3) | 4046 (1) |
| H(2) | −122 | 847 | 440 |
| H(3) | −17 | 1021 | 411 |
| H(6) | 311 | 416 | 446 |
| H(7) | 177 | 244 | 410 |

Table 4. *Bond lengths* (Å) *and angles* (°)

These values are not corrected for thermal motion. The e.s.d.'s are about 0·005 Å for C−C and C−N and 0·01 Å for C=C and C=O, and 1° for all angles.

| | Molecule *A* | Molecule *B* | Molecule *C* | Mean |
|---|---|---|---|---|
| N(1)–N(2) | 1·428 | 1·425 | 1·432 | 1·43 |
| C(1)–N(1) | 1·397 | 1·423 | 1·414 | |
| C(8)–N(1) | 1·426 | 1·397 | 1·425 | |
| C(4)–N(2) | 1·431 | 1·425 | 1·428 | |
| C(5)–N(2) | 1·411 | 1·423 | 1·423 | 1·42 |
| C(1)–O(1) | 1·226 | 1·208 | 1·207 | |
| C(4)–O(2) | 1·199 | 1·207 | 1·207 | |
| C(5)–O(3) | 1·221 | 1·213 | 1·208 | |
| C(8)–O(4) | 1·200 | 1·204 | 1·209 | 1·21 |
| C(1)–C(2) | 1·465 | 1·463 | 1·463 | |
| C(3)–C(4) | 1·461 | 1·453 | 1·476 | |
| C(6)–C(5) | 1·464 | 1·453 | 1·450 | |
| C(7)–C(8) | 1·459 | 1·448 | 1·472 | 1·46 |
| C(2)–C(3) | 1·313 | 1·321 | 1·312 | |
| C(6)–C(7) | 1·330 | 1·300 | 1·324 | 1·32 |
| O(1)···O(4) | 2·666 | 2·600 | 2·636 | |
| O(2)···O(3) | 2·646 | 2·663 | 2·640 | 2·65 |
| C(1)···C(8) | 2·467 | 2·466 | 2·471 | |
| C(4)···C(5) | 2·469 | 2·470 | 2·477 | 2·47 |
| C(1)–N(1)–C(8) | 121·9 | 122·0 | 121·0 | |
| C(4)–N(2)–C(5) | 120·6 | 120·3 | 120·7 | 121 |
| C(1)–N(1)–N(2) | 118·7 | 120·1 | 118·5 | |
| C(8)–N(1)–N(2) | 119·4 | 118·0 | 119·8 | |
| C(4)–N(2)–N(1) | 120·0 | 119·7 | 119·4 | |
| C(5)–N(2)–N(1) | 119·4 | 119·5 | 120·0 | 119·5 |
| N(1)–C(1)–O(1) | 121·4 | 120·5 | 121·5 | |
| N(1)–C(8)–O(4) | 121·1 | 120·7 | 120·4 | |
| N(2)–C(4)–O(2) | 121·1 | 120·8 | 121·2 | |
| N(2)–C(5)–O(3) | 121·3 | 120·7 | 120·3 | 121 |
| C(2)–C(1)–O(1) | 121·4 | 123·8 | 122·4 | |
| C(3)–C(4)–O(2) | 123·8 | 123·4 | 124·3 | |
| C(6)–C(5)–O(3) | 122·4 | 123·2 | 123·2 | |
| C(7)–C(8)–O(4) | 123·4 | 122·3 | 123·8 | 123 |
| N(1)–C(1)–C(2) | 117·2 | 115·7 | 115·9 | |
| N(1)–C(8)–C(7) | 115·4 | 117·0 | 115·8 | |
| N(2)–C(4)–C(3) | 115·0 | 115·7 | 114·4 | |
| N(2)–C(5)–C(6) | 116·3 | 116·1 | 116·4 | 116 |
| C(1)–C(2)–C(3) | 122·4 | 123·1 | 122·7 | |
| C(4)–C(3)–C(2) | 121·8 | 121·7 | 122·3 | |
| C(5)–C(6)–C(7) | 122·1 | 121·1 | 122·5 | |
| C(8)–C(7)–C(6) | 122·1 | 123·1 | 122·3 | 122 |

dial-setting 150. At 80 °C the crystals no longer extinguished polarized light and signs of surface decomposition were visible; by 120 °C the material appeared to have vitrified and the surface of the blackened solid was bubbling, indicating complete decomposition of the compound.

It was evident from the Wilson plot that the calculated values of 2·15 Å$^2$ for $B$ and 0·45 for the scale factor were not the best possible values. As an experiment, a new set of $E$'s was generated assuming $B = 3{\cdot}5$ Å$^2$ and a scale factor 0·4. The 380 largest $E$'s were used in *SAYRE* with the same starting set of reflexions as before (Table 2). One solution was markedly better than any other (consistency index 0·72). It started with the correct set of signs but that of $\bar{8},5,11$ had been

Table 5. *Least-squares planes and torsion angles*

(*a*) Four-atom planes

| | Atoms defining the plane and deviations from it (Å) | | | | | | Direction cosines of the normal to the plane referred to | | |
|---|---|---|---|---|---|---|---|---|---|
| | C(1) | C(8) | N(1) | N(2) | C(4) | C(5) | *a* | *b* | *c** |
| Molecule *A* | 0·00 | 0·00 | 0·01 | 0·00 | −0·58 | 0·56 | 0·160 | −0·302 | 0·940 |
| *B* | 0·00 | 0·00 | −0·01 | 0·00 | −0·44 | 0·61 | −0·019 | −0·326 | 0·945 |
| *C* | 0·02 | 0·02 | −0·05 | 0·02 | −0·53 | 0·61 | 0·118 | −0·201 | 0·972 |
| Molecule *A* | 0·55 | −0·58 | 0·00 | 0·00 | 0·00 | 0·00 | −0·138 | 0·061 | 0·988 |
| *B* | 0·58 | −0·47 | 0·01 | 0·04 | 0·01 | 0·01 | 0·243 | 0·028 | 0·970 |
| *C* | 0·65 | −0·48 | 0·00 | 0·00 | 0·00 | 0·00 | −0·221 | 0·131 | 0·966 |

(*b*) Fourteen-atom planes with atom deviations (Å)

| Molecule | N(1) | N(2) | O(1) | O(2) | O(3) | O(4) | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *A* | 0·00 | 0·00 | 0·54 | −0·66 | 0·54 | −0·64 | 0·27 | 0·23 | −0·08 | −0·31 | 0·29 | 0·22 | −0·10 | −0·30 |
| *B* | −0·05 | −0·08 | 0·40 | −0·70 | 0·56 | −0·55 | 0·24 | 0·30 | 0·02 | −0·30 | 0·27 | 0·23 | −0·08 | −0·26 |
| *C* | −0·08 | −0·03 | 0·56 | −0·61 | 0·59 | −0·59 | 0·29 | 0·22 | −0·12 | −0·31 | 0·28 | 0·19 | −0·11 | −0·30 |

Direction cosines: *A* 0·015, −0·128, 0·992; *B* 0·098, −0·158, 0·982; *C* −0·048, −0·030, 0·998.

(*c*) Torsion angles (°)

| Molecule | C(1)–N(1)–N(2)–C(4) | C(5)–N(2)–N(1)–C(8) |
|---|---|---|
| *A* | 26·4 | 28·3 |
| *B* | 22·3 | 28·3 |
| *C* | 32·3 | 22·3 |

reversed during the cycling. The $E$ map clearly showed the molecule at $z = \frac{1}{4}$ but the images of those at $z = \frac{1}{12}$ and $\frac{5}{12}$ were scrambled. The process was repeated with NBACK = 0, but with no success. A different starting set was tried (Table 2). The best solutions had consistency indices of about 0·61 and the $E$ maps showed only scrambled images of the molecules. This starting set was now used with the original set of $E$'s but the best solution was not correct. At this stage an error was made in the sorting of the reflexions for the starting set and two of the same parity group were used to define the origin. One solution from this set had a consistency index of 0·68 and proved to be identical with the correct set of signs that had been found before. In the process, the sign of the one variable (242) had again been reversed by the program.

The effect of choosing a larger $B$ for calculating the $E$'s is subtle. Not only are all the $E$'s increased in magnitude but the order is also affected, the largest effects being felt for the reflexions at high $\theta$ angle, with the largest $h$, $k$ and $l$ indices.

The problems involved in getting the best estimate of the overall isotropic thermal parameter have been reviewed by Rogers (1965), and the effect of using an incorrect value of $B$ to calculate the $E$'s has been discussed by Dewar (1968). It is not clear which was the most damaging in this case: wrong $B$ and hence $E$'s, wrong order in which the $E$'s were added into the $\Sigma_2$ calculations, or including in the starting set reflexions involved in too few $\Sigma_2$ triplets.

## Discussion

### *Molecular geometry*

The three independent molecules in the asymmetric unit have, for all practical purposes, identical geometry (Tables 4 and 5). DIAZAN is distinctly non-planar and has the approximate symmetry 222. The distortion of the molecule is best described as a twisting of the two halves of the molecule in opposite senses about the N–N bond until the (O)C–N–N–C(O) torsion angle within each six-membered ring is approximately 25°. (See Table 5 for the six C–N–N–C torsion angles.) The force causing this distortion could well be the repulsions between the pairs O(1)/O(4) and O(2)/O(3). These O···O separations lie between 2·60 and 2·67 Å compared with 2·46 to 2·48 Å between the C atoms to which they are bonded. Were the molecule exactly planar, the O atoms would be forced together, thus producing large compression strains. This energetically unfavourable situation is found in the geometrically comparable molecule naphthazarin (Pascard-Billy, 1962; Cradwick & Hall, 1971). Here the very strong intramolecular O···H···O bond holds the pair of O atoms together (O···O distances lie between 2·57 and 2·62 Å, C···C between 2·48 and 2·49 Å) which results in the internal C–C–O angles [equivalent to N(1)–C(1)–O(1) in DIAZAN] being slightly larger (between 121 and 122°) than the external C–C–O angles, which are between 119 and 120°. In DIAZAN, the inner

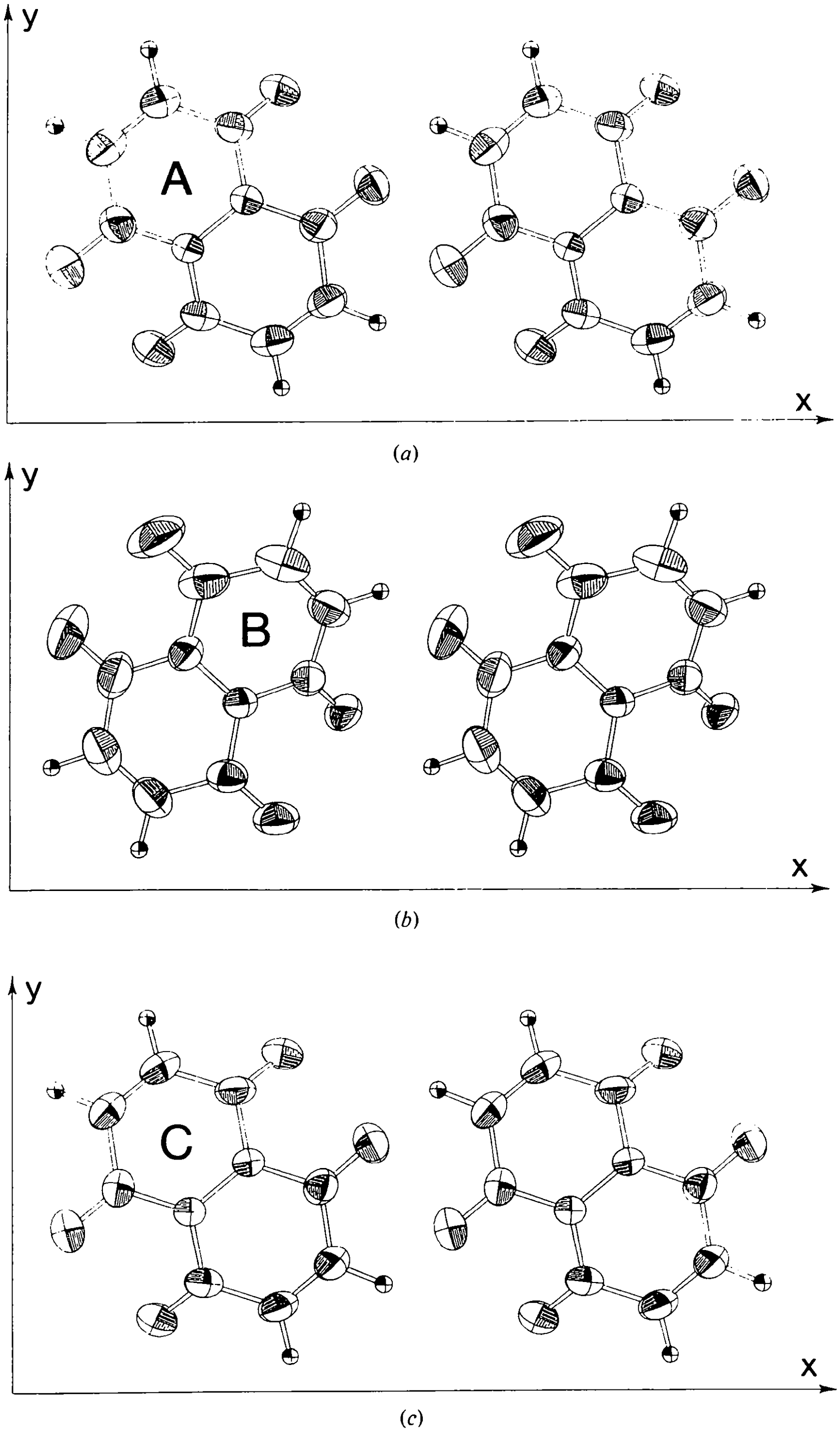

Fig. 4. Stereoscopic views of molecules *A*, *B* and *C*, projected onto the *xy* plane, showing the ellipsoids of thermal vibration. The overall thermal motion is similar for molecules *A* and *C*; the motion of molecule *B* is distinctly larger. None of the molecules is well fitted by the rigid-body approximation, while within any one molecule the four O atoms differ considerably in their amplitudes of vibration. The r.m.s. amplitudes of vibration (in Å) parallel to the principal axes of their thermal ellipsoids are given below for some representative atoms:

O(1),*A*: 0·34 × 0·27 × 0·20. O(1),*B*: 0·42 × 0·29 × 0·19.
O(2),*B*: 0·33 × 0·24 × 0·19. O(3),*C*: 0·29 × 0·24 × 0·19.
C(3),*A*: 0·27 × 0·24 × 0·19. C(2),*B*: 0·33 × 0·25 × 0·20.

N–C–O angles lie between 120 and 121°, while the outer ones are systematically larger, between 121 and 124°.

The two N atoms in the molecule are best described as $sp^2$-hybridized, as C(1), C(8), N(1) and N(2) (or their equivalents) are coplanar (Table 5).

Because the asymmetric unit consists of three chemically identical yet crystallographically unique molecules, there are several independent measures of the same bond lengths, *e.g.* 3 for N–N, 12 for C–N and C–C, and 6 for C=C. The range of lengths observed for these bonds gives a good measure of the probable accuracy and reliability of the parameters (as opposed to their precision) derived from the structural analysis. The lengths in Table 4 show that the range of results is disappointingly large, doubtless due to the relatively large and anisotropic thermal motion. However, the mean lengths do allow some conclusions to be drawn. The N–N length should be compared with the values found in 1,2-dimethyl-3,6-pyridazinedione (Otterson, 1973) and in 2,4-diphenyl-2,3-benzodiazocin-1(2*H*)-one (Harlow & Simonsen, 1976). Both compounds have the arrangement O=C–N(C)–N and the N–N lengths were relatively long in both cases: 1·406 and 1·441 Å respectively. The bond order of N–N in DIAZAN is *less* than 1 (Allmann, 1975; Burke-Laing & Laing, 1976) while the bond orders for C–N and C–C are both close to 1·1. The C=C bonds are effectively isolated double bonds.

The centrosymmetry of naphthazarin and the equivalence of the 1, 4, 5 and 8 C atoms in it have recently been demonstrated by Kobayashi, Terui, Tori & Tsuji (1976) with $^{13}C$ NMR techniques. They concluded that naphthazarin has a delocalized electronic structure. Comparison of $^{13}C$ shifts shows that the character of the C=C moiety in DIAZAN is between that in 1,4-naphthaquinone and that in naphthazarin. The $\delta_C$ shifts are: 1,4-naphthaquinone 138·5; DIAZAN 135·8; naphthazarin 134·6. These results are in accord with the crystallographic results, which show that C=C bonds are essentially isolated in both naphthazarin (Cradwick & Hall, 1971) and 1,4-naphthaquinone (Gaultier & Hauw, 1965).

It appears, therefore, that what delocalization is present in DIAZAN is confined to the (H)C–C(=O)–N–C(=O)–C(H) chain, and the bonding is similar in character to that found in simple amides. Judged by the criteria given by Lewis & Peters (1975), DIAZAN is *not* aromatic.

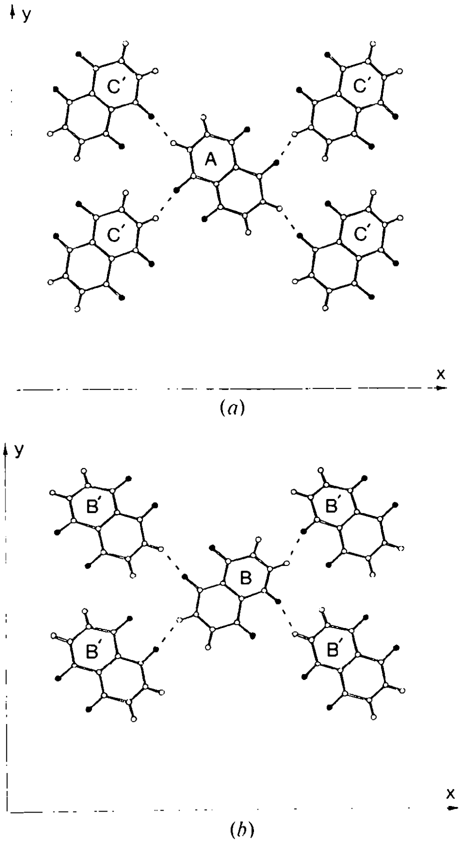

Fig. 5. The packing of the molecules showing the C=O···H–C contacts. (*a*) The layer at $z = \frac{1}{12}$. (*b*) The layer at $z = \frac{1}{4}$. The O···H separations given in Table 6 are indicated by the dashed lines. The O atoms are shown as solid circles.

*Packing*

There are two different types of layer: that at $z = \frac{1}{12}$ (equivalent to that at $z = \frac{5}{12}$) containing molecules *A*

Table 6. *Short intermolecular* O···C *separations* (Å)

(*a*) Within a layer; C=O···H–C

| Atom in asymmetric unit | to atom | in position | Distance | O···H separation |
|---|---|---|---|---|
| C(2), *A* | O(1), *C* | 3 | 3·11 | 2·5 |
| O(1), *A* | C(2), *C* | 3(010) | 3·04 | 2·3 |
| C(6), *A* | O(3), *C* | 3(110) | 3·08 | 2·3 |
| O(3), *A* | C(6), *C* | 3(100) | 3·09 | 2·4 |
| O(4), *B* | C(7), *B* | 3 | 2·99 | 2·1 |
| O(2), *B* | C(3), *B* | 3(110) | 3·10 | 2·4 |
| C(3), *B* | O(2), *B* | 3(100) | 3·10 | 2·4 |
| C(7), *B* | O(4), *B* | 3(010) | 2·99 | 2·1 |

(*b*) Between layers; C=O···C=O

| Atom in asymmetric unit | to atom | in position | Distance |
|---|---|---|---|
| O(1), *A* | C(4), *B* | 1 | 3·14 |
| C(8), *A* | O(2), *B* | 1 | 3·10 |
| O(1), *B* | C(5), *C* | 1 | 3·05 |
| C(4), *A* | O(3), *C* | 4(01$\bar{1}$) | 2·97 |
| O(3), *A* | C(5), *B* | 3(100) | 2·90 |
| C(5), *A* | O(3), *B* | 3(100) | 3·17 |
| C(8), *C* | O(1), *C* | 2(011) | 3·18 |
| C(1), *C* | O(1), *C* | 2(011) | 3·19 |

Equivalent positions
(1) $x, y, z$
(2) $-x, -y, -z$
(3) $-x, \frac{1}{2}+y, \frac{1}{2}-z$
(4) $x, \frac{1}{2}-y, \frac{1}{2}+z$

and $C$; and that at $z = \frac{1}{4}$ containing pairs of molecule $B$ related by the $2_1$ screw axis (Fig. 5). Within each layer every molecule is involved in four short C···O separations (between 2·9 and 3·2 Å) of the type which Donohue (1968) describes as *not* C–H···O=C hydrogen bonds. Between the layers there are also O···C contacts, in all cases involving C atoms which are labelled + in (I), *i.e.* which carry a small positive charge relative to the O, N and C atoms bonded to them (Table 6).

Prout & Kamenar (1973) have described in detail the various modes of packing in molecular complexes and have discussed the structures which are formed when $\pi$–$\pi^*$ electronic interactions predominate. The interlayer forces found in DIAZAN are comparable with those found in molecular complexes of benzoquinone but the C···O separations in the DIAZAN case are generally shorter. It appears that DIAZAN is self-complexing, resulting in the formation of the unit of three molecules in the crystal.

The high density of the crystals, 1·58 g cm$^{-3}$, compared with the value of 1·3 g cm$^{-3}$ commonly found for organic crystals (Laing, 1975), is typical of aromatic compounds or compounds with a large proportion of O atoms and hydrogen bonds; *e.g.* naphthazarin, which is trimorphic, with $D$ between 1·53 and 1·58 g cm$^{-3}$ (Pascard-Billy, 1962), and sucrose with $D$ = 1·59 g cm$^{-3}$. The effective volume of each non-hydrogen atom in DIAZAN is only 14·1 Å$^3$, yet the average volume per atom including hydrogens is 11·0 Å$^3$. Both volumes are far from the typical values of 18 and 8·9 Å$^3$ reported by Kempster & Lipson (1972) and Srinivasan & Rajan (1975) respectively. This anomaly is caused by the H atoms constituting such a small fraction of the total number of atoms in the molecule.

## Conclusion

One must conclude that DIAZAN is not aromatic in the generally accepted sense of the word and that it is the large attractive forces between the molecules associated with the short interlayer O···C separations and short intralayer C=O···H–C separations which account for the stability of the material in the solid state.

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