

## The Crystal and Molecular Structure of Tricycloquinazoline

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The crystal structure of tricycloquinazoline has been determined by the use of the  $h0l$  weighted reciprocal lattice, and a trial-and-error computer program to find the molecular position in the unit cell. The unit cell is monoclinic with dimensions  $a=16.51$ ;  $b=3.873$ ;  $c=23.50$  Å;  $\beta=105.7^\circ$ . The space group is  $P2_1/c$ , with four molecules per unit cell. Data were collected photographically with Cu  $K\alpha$  radiation. The atomic coordinates and anisotropic temperature parameters were refined by least-squares to a final  $R$  value of 0.068 for 828 observed reflexions. The molecule is planar within  $\pm 0.05$  Å and shows a threefold rotation axis perpendicular to the mean plane of the molecule.

### Introduction

The carcinogenic compound tricycloquinazoline (TCQ, see Fig. 1) was synthesized in the Department of Pharmaceutical Chemistry at Nottingham University (Cooper & Partridge, 1954) and its biological properties were studied at the Cancer Research Laboratories in that University (Baldwin, Cunningham & Partridge, 1959; Baldwin, Palmer & Partridge, 1962). It is of particular interest because it is structurally different from the cancer-producing aromatic hydrocarbons and because the biological activity of its derivatives is greatly dependent upon their overall shape, position of substituents, and number of nitrogen atoms (Baldwin, Cunningham, Dean, Partridge & Surteas, 1965). Japanese workers have discussed the possible interaction of TCQ with deoxyribonucleic acid (Nagata, Kodama, Immaura & Tagashire, 1966).

### Experimental

Considerable difficulty was experienced in obtaining a suitable crystal for X-ray examination from the material which was kindly provided by Professor Partridge. The compound was recrystallized from a variety of organic solvents and the best samples came from a 3:1 mixture of pyridine:benzene. The crystals were in the form of yellow needles up to 5 mm long but very thin, about 0.1 mm in cross section. Many of the crystals had grown in clusters and tapered to a point. It was found to be very difficult to cut the crystals without shattering them completely. In addition it was found that many crystals which showed clear extinction under the polarizing microscope, were, in fact, split when examined by X-ray photographs. Because of these factors the photographic data were collected from one uncut needle, which showed several satellite reflexions.

The unit cell was measured by calibration of the zero layer Weissenberg photograph of the needle axis with

NaCl powder lines. This axis was the  $b$  axis of a monoclinic cell with dimensions:

$$a = 16.51 \pm 0.01 \text{ \AA}, \quad b = 3.873 \pm 0.003 \text{ \AA}, \\ c = 23.50 \pm 0.01 \text{ \AA}, \quad \beta = 105.7 \pm 0.2^\circ \quad (\text{at } 20^\circ\text{C})$$

Measured density =  $1.471 \pm 0.002 \text{ g.cm}^{-3}$ .  
Calculated density = 1.469 with four molecules per unit cell. The length of the  $b$  axis was measured on a four-circle diffractometer, and the density was obtained by flotation in a calibrated density gradient column.

Equi-inclination Weissenberg photographs were taken for the  $b$  axis layers 0, 1, 2, with Cu  $K\alpha$  radiation.

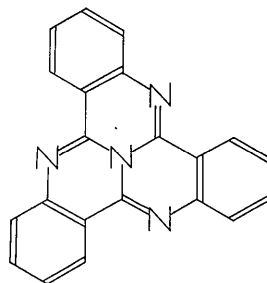


Fig. 1. Tricycloquinazoline (TCQ).

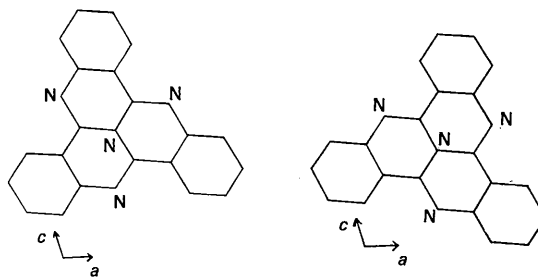


Fig. 2. Two possible molecular orientations having the same orientation of the benzene rings.

The Leeds-Cox camera had a unidimensional integration device. The film intensities were measured with a Joyce-Loebl recording microdensitometer except

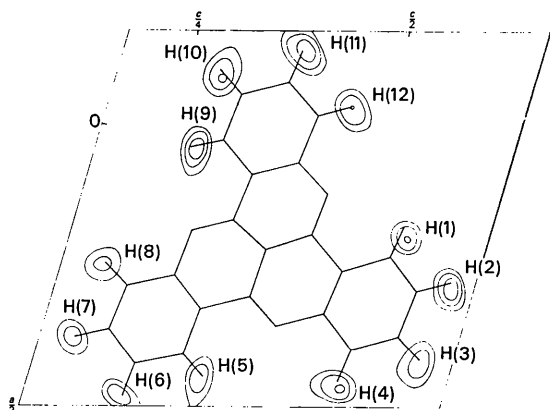


Fig. 3. Superimposed sections of the final three-dimensional electron density map, with contours at an interval of  $1 \text{ e.}\text{\AA}^{-3}$  starting at  $3 \text{ e.}\text{\AA}^{-3}$ .

for the very weak reflexions which were visually estimated. Independent measurement of each symmetrically related reflexion was undertaken and values for  $hkl$  were averaged with the  $\bar{h}\bar{k}\bar{l}$  measurements. No correction for absorption was applied. The intensities for different layers were scaled by means of measurements of the stronger reflexions taken on a Hilger-Watts linear diffractometer. Altogether 828 reflexions were observed out of the 3410 possible with copper radiation.

The systematic absences showed  $h0l$  reflexions absent when  $l$  was odd, but it was not possible to measure any of the  $0k0$  reflexions except for the  $040$ , which was obtained using the four-circle diffractometer with copper radiation. Thus the space group could not be determined unambiguously but  $P2_1/c$  was clearly more probable than  $P2/c$ .

### Determination of the structure

The  $h0l$  weighted reciprocal lattice showed the familiar hexagonal pattern of peaks characteristic of the benzene ring transform, and the orientation of the benzene rings was thus determined. By consideration of the

Table 1. Fractional coordinates with estimated standard deviations ( $\text{\AA}$ )

|       | $x/a$   | $\sigma(x)$ | $y/b$   | $\sigma(y)$ | $z/c$  | $\sigma(z)$ |
|-------|---------|-------------|---------|-------------|--------|-------------|
| N(1)  | 0.1242  | 0.007       | 0.3677  | 0.009       | 0.4630 | 0.006       |
| N(2)  | 0.3616  | 0.007       | 0.5826  | 0.009       | 0.4444 | 0.006       |
| N(3)  | 0.1880  | 0.007       | 0.0818  | 0.009       | 0.3107 | 0.006       |
| N(4)  | 0.2246  | 0.006       | 0.3422  | 0.008       | 0.4058 | 0.006       |
| C(1)  | 0.1977  | 0.008       | 0.4289  | 0.010       | 0.4571 | 0.007       |
| C(2)  | 0.2613  | 0.008       | 0.6052  | 0.011       | 0.5043 | 0.008       |
| C(3)  | 0.2415  | 0.009       | 0.6970  | 0.011       | 0.5566 | 0.008       |
| C(4)  | 0.3019  | 0.009       | 0.8573  | 0.011       | 0.5999 | 0.008       |
| C(5)  | 0.3814  | 0.009       | 0.9263  | 0.012       | 0.5931 | 0.009       |
| C(6)  | 0.4017  | 0.009       | 0.8361  | 0.012       | 0.5414 | 0.009       |
| C(7)  | 0.3404  | 0.009       | 0.6732  | 0.010       | 0.4964 | 0.008       |
| C(8)  | 0.3072  | 0.009       | 0.4270  | 0.011       | 0.4030 | 0.008       |
| C(9)  | 0.3281  | 0.008       | 0.3322  | 0.010       | 0.3489 | 0.008       |
| C(10) | 0.4064  | 0.009       | 0.4042  | 0.011       | 0.3406 | 0.008       |
| C(11) | 0.4244  | 0.009       | 0.3128  | 0.011       | 0.2888 | 0.009       |
| C(12) | 0.3633  | 0.009       | 0.1488  | 0.011       | 0.2440 | 0.008       |
| C(13) | 0.2855  | 0.009       | 0.0739  | 0.011       | 0.2521 | 0.008       |
| C(14) | 0.2675  | 0.008       | 0.1656  | 0.010       | 0.3048 | 0.008       |
| C(15) | 0.1690  | 0.009       | 0.1692  | 0.010       | 0.3576 | 0.008       |
| C(16) | 0.0862  | 0.008       | 0.0969  | 0.010       | 0.3652 | 0.008       |
| C(17) | 0.0253  | 0.009       | -0.0689 | 0.010       | 0.3200 | 0.008       |
| C(18) | -0.0534 | 0.009       | -0.1268 | 0.012       | 0.3266 | 0.009       |
| C(19) | -0.0724 | 0.009       | -0.0225 | 0.011       | 0.3781 | 0.009       |
| C(20) | -0.0140 | 0.009       | 0.1411  | 0.011       | 0.4236 | 0.008       |
| C(21) | 0.0669  | 0.008       | 0.2016  | 0.010       | 0.4170 | 0.008       |
| H(1)  | 0.182   |             | 0.645   |             | 0.563  |             |
| H(2)  | 0.287   |             | 0.923   |             | 0.639  |             |
| H(3)  | 0.426   |             | 1.053   |             | 0.627  |             |
| H(4)  | 0.462   |             | 0.889   |             | 0.537  |             |
| H(5)  | 0.452   |             | 0.529   |             | 0.374  |             |
| H(6)  | 0.483   |             | 0.361   |             | 0.282  |             |
| H(7)  | 0.377   |             | 0.093   |             | 0.206  |             |
| H(8)  | 0.241   |             | -0.051  |             | 0.218  |             |
| H(9)  | 0.039   |             | -0.142  |             | 0.281  |             |
| H(10) | -0.098  |             | -0.255  |             | 0.292  |             |
| H(11) | -0.132  |             | -0.066  |             | 0.384  |             |
| H(12) | -0.030  |             | 0.218   |             | 0.461  |             |

molecular packing it was possible to narrow the position of the centre of the molecule to within a relatively small region. There were only two possible ways of constructing the molecular model by use of the benzene ring orientation (Fig. 2). The best position of fit of each model to the observed  $h0l$  structure factors was determined by means of a computer program, and then the two corresponding  $h0l$  Fourier electron density syntheses were computed. One of these maps had much better resolution than the other, and it was possible to lower the  $R$  value to 0.136 for the  $h0l$  zone, with use of the Fourier refinement followed by two-dimensional least-squares refinement of the  $x$  and  $z$  coordinates. Every atom was clearly resolved in this projection, and the projected bond lengths were of the expected magnitude.

A reasonable set of  $y$  coordinates was calculated from the projected bond lengths assuming benzene ring bond lengths of 1.40 Å. The position of the molecule in the  $y$  direction was determined with the aid of a computer program written in FORTRAN for an IBM1620. The  $x$  and  $z$  coordinates were kept fixed and their contribution to a set of general  $hkl$  structure factors was calculated and stored assuming the space group  $P2_1/c$ . The molecule was then moved in the  $y$  direction and the structure factors were rapidly calculated using the stored contributions. Because of the symmetry of the space group in projection on the (010) plane, there are two sets of coordinates differing by  $c/4$  in their  $z$  coordinates which give the same  $R$  index for the  $h0l$  reflexions, but different  $R$  indices for the  $hkl$  reflexions. It was necessary, therefore, to examine two positions of the molecule differing by a translation of  $c/4$  in the  $z$  direction, and a clear minimum in the  $R$  index was found for one of these positions. A set of 15 reflexions of large magnitude and low  $\theta$  values gave a minimum  $R$  value of 0.095. When these coordinates were used to calculate structure factors for all the observed reflexions the  $R$  value was 0.208.

### Refinement

The structure was refined by a least-squares program written by Dr G.A. Mair for the IBM1620 machine by use of the block-diagonal approximation. Refinement of the atomic coordinates and isotropic temperature parameters gave an  $R$  value of 0.129 after 5 cycles. The positions of the hydrogen atoms were calculated for a C-H bond length of 1.05 Å. The hydrogen atoms were given isotropic  $B$  values of 3.5 Å<sup>2</sup> and their parameters were not refined. At this stage the scale factors for the layers  $h0l$ ,  $h1l$  and  $h2l$  were checked and slightly adjusted, and then they were not altered during the remaining refinement cycles. The weighting scheme used was of the form

$$\sqrt{w} = \sqrt{[P^2 / (P^2 + (F_o - Q)^2)]},$$

with the values  $P=24$  and  $Q=15$ , which were chosen so as to represent the estimated accuracy of the photo-

graphic data. Four cycles of refinement with anisotropic temperature parameters lowered the  $R$  value from 0.1200 to 0.0678.

A three-dimensional electron density map was calculated with the phases from the final set of parameters and Dr Mair's program for the IBM1620 (Fig. 3). The hydrogen atoms were then omitted and a difference-Fourier synthesis was calculated (Fig. 4).

A list of the observed and calculated structure factors is available on request from the authors.

### Discussion

The final atomic coordinates are given in Table 1, and the final temperature parameters in Table 2. The bond lengths and bond angles are given in Tables 3 and 4. Because the chemical formula indicates a threefold rotation axis perpendicular to the molecular plane, the mean values of chemically equivalent bond lengths and angles were calculated and they are also given in Tables 3 and 4 together with their standard deviations from the mean (see Fig. 5).

Table 2. Temperature parameters ( $b_{ij}$ )  $\times 10^4$

$$T(hkl) = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)].$$

|       | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{23}$ | $b_{13}$ | $b_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| N(1)  | 406      | 6639     | 158      | 356      | 175      | 146      |
| N(2)  | 449      | 7526     | 152      | 189      | 157      | 263      |
| N(3)  | 439      | 7730     | 180      | -257     | 191      | 339      |
| N(4)  | 339      | 5320     | 168      | 200      | 178      | 233      |
| C(1)  | 419      | 6448     | 128      | 489      | 131      | 581      |
| C(2)  | 402      | 5397     | 175      | 465      | 102      | 253      |
| C(3)  | 467      | 6948     | 160      | 100      | 73       | -114     |
| C(4)  | 541      | 6511     | 179      | 129      | 162      | 459      |
| C(5)  | 437      | 7792     | 232      | -45      | 72       | 355      |
| C(6)  | 465      | 6767     | 222      | 407      | 146      | 274      |
| C(7)  | 438      | 5103     | 165      | 111      | 120      | 270      |
| C(8)  | 440      | 5839     | 192      | 363      | 141      | 29       |
| C(9)  | 421      | 5334     | 186      | 451      | 197      | 345      |
| C(10) | 407      | 7827     | 215      | 532      | 174      | 600      |
| C(11) | 433      | 8032     | 231      | 577      | 290      | 673      |
| C(12) | 555      | 7986     | 174      | 632      | 283      | 1030     |
| C(13) | 436      | 8693     | 152      | 242      | 173      | 809      |

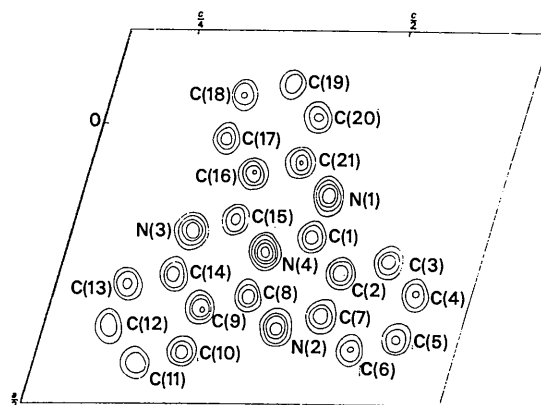


Fig. 4. Superimposed sections of the three-dimensional difference electron density map, with contours at 0.1 e.Å<sup>-3</sup> starting at 0.2 e.Å<sup>-3</sup>.

Table 2 (cont.)

|       |     |      |     |      |     |      |
|-------|-----|------|-----|------|-----|------|
| C(14) | 406 | 5695 | 184 | 331  | 260 | 497  |
| C(15) | 402 | 5852 | 178 | -181 | 135 | 176  |
| C(16) | 368 | 5510 | 190 | 416  | 172 | 492  |
| C(17) | 452 | 4752 | 204 | -443 | 176 | -467 |
| C(18) | 391 | 8073 | 221 | -125 | 120 | 25   |
| C(19) | 424 | 7446 | 269 | 275  | 189 | -160 |
| C(20) | 440 | 6771 | 191 | 230  | 249 | 253  |
| C(21) | 398 | 4159 | 148 | 227  | 76  | -178 |

The threefold symmetry is followed to within the experimental error. The best least-squares mean plane was calculated by the method of Schomaker, Waser, Marsh & Bergman (1959); firstly, through all the atoms, and then through each of the three quina-

zoline groups (Table 5). There does not seem to be any significant difference in orientation between these planes.

A calculation of the intermolecular contacts showed that the closest approaches, which are summarized in Table 6, occurred between molecules related by a translation  $\pm b$ . All contacts were of the usual van der Waals magnitude. A diagram of the structure viewed along the  $b$  axis (see Fig. 6) shows that the tightly packed columns of molecules in the  $b$  direction have little inter-  
action with each other and there are gaps running parallel to the (100) and (10 $\bar{2}$ ) planes which account for the tendency of the crystals to split in the direction of the needle axis.

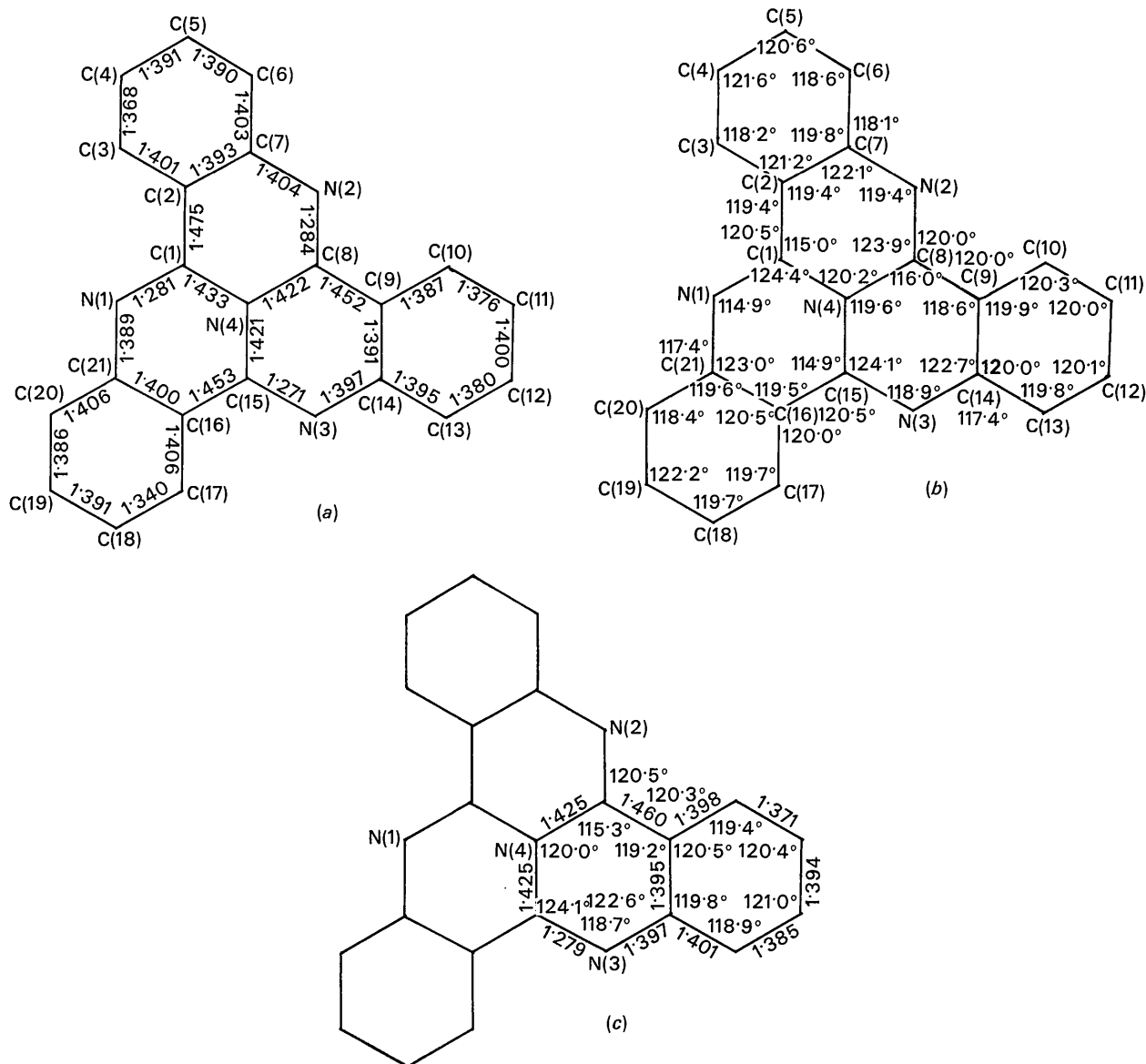


Fig. 5. (a) Bond lengths (Å) and (b) angles (°) for the final coordinates, together with (c) the mean values for chemically equivalent bonds and angles.

Table 3. Bond lengths of TCQ ( $R=0.0678$ ), with mean values

| Standard deviations are given in parenthesis. |       |               | Standard deviations are given in parenthesis. |       |               |
|---|-------|---------------|---|-------|---------------|
| Bond  | (Å)   | Mean          | Bond  | (Å)   | Mean          |
| N(4)–C(1)                                     | 1.433 |               | C(3)–C(4)                                     | 1.368 |               |
| N(4)–C(8)                                     | 1.422 | 1.425 (0.007) | C(10)–C(11)                                   | 1.376 | 1.371 (0.004) |
| N(4)–C(15)                                    | 1.421 |               | C(17)–C(18)                                   | 1.370 |               |
| N(1)–C(1)                                     | 1.281 |               | C(4)–C(5)                                     | 1.391 |               |
| N(2)–C(8)                                     | 1.284 | 1.279 (0.007) | C(11)–C(12)                                   | 1.400 | 1.394 (0.005) |
| N(3)–C(15)                                    | 1.271 |               | C(18)–C(19)                                   | 1.391 |               |
| N(1)–C(21)                                    | 1.389 |               | C(2)–C(3)                                     | 1.401 |               |
| N(2)–C(7)                                     | 1.404 | 1.397 (0.008) | C(9)–C(10)                                    | 1.387 | 1.398 (0.010) |
| N(3)–C(14)                                    | 1.397 |               | C(16)–C(17)                                   | 1.406 |               |
| C(1)–C(2)                                     | 1.475 |               | C(5)–C(6)                                     | 1.390 |               |
| C(8)–C(9)                                     | 1.452 | 1.460 (0.013) | C(12)–C(13)                                   | 1.380 | 1.385 (0.005) |
| C(15)–C(16)                                   | 1.453 |               | C(19)–C(20)                                   | 1.386 |               |
| C(2)–C(7)                                     | 1.393 |               | C(6)–C(7)                                     | 1.403 |               |
| C(9)–C(14)                                    | 1.391 | 1.395 (0.005) | C(13)–C(14)                                   | 1.395 | 1.401 (0.006) |
| C(16)–C(21)                                   | 1.400 |               | C(20)–C(21)                                   | 1.406 |               |

Table 4. Bond angles for TCQ(°)

| Standard deviations in parentheses. |       |             | Standard deviations in parentheses. |       |             |
|-------------------------------------|-------|-------------|-------------------------------------|-------|-------------|
| Bond angle                          | (deg) | Mean        | Bond angle                          | (deg) | Mean        |
| C(21)–N(1)–C(1)                     | 117.9 |             | C(2)–C(3)–C(4)                      | 118.2 |             |
| C(7)–N(2)–C(8)                      | 119.4 | 118.7 (0.8) | C(9)–C(10)–C(11)                    | 120.3 | 119.4 (1.1) |
| C(14)–N(3)–C(15)                    | 118.9 |             | C(16)–C(17)–C(18)                   | 119.7 |             |
| C(1)–N(4)–C(8)                      | 120.2 |             | C(3)–C(4)–C(5)                      | 121.6 |             |
| C(8)–N(4)–C(15)                     | 119.6 | 120.0 (0.3) | C(10)–C(11)–C(12)                   | 120.0 | 120.4 (1.0) |
| C(15)–N(4)–C(1)                     | 120.1 |             | C(17)–C(18)–C(19)                   | 119.7 |             |
| N(1)–C(1)–C(2)                      | 120.5 |             | C(4)–C(5)–C(6)                      | 120.6 |             |
| N(2)–C(8)–C(9)                      | 120.0 | 120.5 (0.5) | C(11)–C(12)–C(13)                   | 120.1 | 121.0 (1.1) |
| N(3)–C(15)–C(16)                    | 121.0 |             | C(18)–C(19)–C(20)                   | 122.2 |             |
| N(1)–C(1)–N(4)                      | 124.4 |             | C(5)–C(6)–C(7)                      | 118.6 |             |
| N(2)–C(8)–N(4)                      | 123.9 | 124.1 (0.3) | C(12)–C(13)–C(14)                   | 119.8 | 118.9 (0.8) |
| N(3)–C(15)–N(4)                     | 124.1 |             | C(19)–C(20)–C(21)                   | 118.4 |             |
| N(4)–C(1)–C(2)                      | 115.0 |             | C(6)–C(7)–N(2)                      | 118.1 |             |
| N(4)–C(8)–C(9)                      | 116.0 | 115.3 (0.6) | C(13)–C(14)–N(3)                    | 117.3 | 117.6 (0.4) |
| N(4)–C(15)–C(16)                    | 114.9 |             | C(20)–C(21)–N(1)                    | 117.4 |             |
| C(1)–C(2)–C(3)                      | 119.4 |             | C(2)–C(7)–N(2)                      | 122.1 |             |
| C(8)–C(9)–C(10)                     | 121.5 | 120.3 (1.1) | C(9)–C(14)–N(3)                     | 122.7 | 122.6 (0.5) |
| C(15)–C(16)–C(17)                   | 120.0 |             | C(16)–C(21)–N(1)                    | 123.0 |             |
| C(1)–C(2)–C(7)                      | 119.4 |             | C(6)–C(7)–C(2)                      | 119.8 |             |
| C(8)–C(9)–C(14)                     | 118.6 | 119.2 (0.5) | C(13)–C(14)–C(9)                    | 120.0 | 119.8 (0.2) |
| C(15)–C(16)–C(21)                   | 119.5 |             | C(20)–C(21)–C(16)                   | 119.6 |             |
| C(3)–C(2)–C(7)                      | 121.2 |             |                                     |       |             |
| C(10)–C(9)–C(14)                    | 119.9 | 120.5 (0.9) |                                     |       |             |
| C(17)–C(16)–C(21)                   | 120.5 |             |                                     |       |             |

Table 5. Least-squares planes with deviations (Å)

| Deviations from mean plane through all atoms |          |       |          |       |          |
|--|----------|-------|----------|-------|----------|
|  | $\Delta$ |       | $\Delta$ |       | $\Delta$ |
| N(1)   | 0.013    | C(6)  | -0.004   | C(15) | -0.037   |
| N(2)   | 0.010    | C(7)  | 0.006    | C(16) | -0.035   |
| N(3)   | -0.052   | C(8)  | -0.009   | C(17) | -0.036   |
| N(4)   | -0.014   | C(9)  | -0.002   | C(18) | 0.008    |
| C(1)   | -0.006   | C(10) | 0.018    | C(19) | 0.046    |
| C(2)   | 0.006    | C(11) | 0.030    | C(20) | 0.045    |
| C(3)   | -0.002   | C(12) | 0.033    | C(21) | 0.004    |
| C(4)   | -0.004   | C(13) | 0.003    |       |          |
| C(5)   | -0.010   | C(14) | -0.015   |       |          |

Table 5 (cont.)

| Equation of plane  |
|--|
| $-0.3269x' + 0.8873y' - 0.3252z' + 2.743 = 0$  |
| Equations of planes through the three quinazoline groups                               |
| $-0.3285x' + 0.8869y' - 0.3249z' + 2.751 = 0$  |
| $-0.3419x' + 0.8833y' - 0.3208z' + 2.794 = 0$  |
| $-0.3145x' + 0.8842y' - 0.3453z' + 2.909 = 0$  |
| [ $x'$ is perpendicular to (100), $y'$ is parallel to $b$ , $z'$ is parallel to $c$ ]. |

Table 6. *Short intermolecular distances* (Å)

| Molecule <i>I</i> | Molecule <i>J</i> | Position | $d_{ij}$ |
|-------------------|-------------------|----------|----------|
| N(1)              | C(21)             | <i>a</i> | 3.45     |
| N(2)              | C(8)              | <i>a</i> | 3.46     |
| N(4)              | C(15)             | <i>a</i> | 3.44     |
| C(1)              | C(2)              | <i>b</i> | 3.45     |
| C(3)              | C(4)              | <i>b</i> | 3.47     |
| C(6)              | C(7)              | <i>a</i> | 3.47     |
| C(9)              | C(14)             | <i>a</i> | 3.45     |
| C(11)             | C(12)             | <i>a</i> | 3.47     |
| C(16)             | C(17)             | <i>a</i> | 3.46     |
| C(19)             | C(20)             | <i>b</i> | 3.46     |

Position of molecule *J*

- (*a*)  $x, y+1, z$   
 (*b*)  $x, y-1, z$

It was expected that the molecule would show rigid body motion in the crystal as has been found for similar molecules. The temperature parameters were therefore analysed using the program written by Dr J. T. McMullan for the IBM1620, as reported by Burns, Ferrier & McMullan, 1967. A comparison between the observed and calculated values of  $U_{ij}$  shows general agreement in magnitude (Table 7). However, it was found on more detailed analysis that the molecule can not be considered to be behaving strictly as a rigid body within the criteria suggested by the above authors. This may be due to the rather limited reflexion data available because of the experimental difficulties.

A noteworthy feature of the molecule is the arrangement of short and long C–N bonds in the central rings. In particular the short value of 1.279 Å with a standard deviation of 0.007 Å seems to be shorter

than is usually observed in heterocyclic rings. For example, some of the shorter values reported are found in adenosine-5'-phosphate and deoxyadenosine, namely 1.312 and 1.317 Å (Kraut & Jensen, 1963; Watson, Sutor & Tollin, 1965). If the covalent Kekulé structures are examined for TCQ it is found that there are 8 structures having the arrangement of double bonds shown in Fig. 7(*a*), and there is only one structure with the alternative arrangement of Fig. 7(*b*). This suggests that the bond order for the bonds shown as C=N in Fig. 7(*a*) should be approaching the value 2, and the observed short bond length agrees with the bond order bond length curve as given by Lofthus (1959) in this respect. However, it is noted that Lofthus used an assumed value of 1.274 Å for a C–N bond with a bond order of 2.

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Table 7. *Observed and calculated  $U_{ij}$  for TCQ* ( $\times 10^4$ )

|       | $U_{11}$ |      | $U_{22}$ |      | $U_{33}$ |      | $U_{23}$ |      | $U_{13}$ |      | $U_{12}$ |      |
|-------|----------|------|----------|------|----------|------|----------|------|----------|------|----------|------|
|       | Obs      | Calc | Obs      | Calc | Obs      | Calc | Obs      | Calc | Obs      | Calc | Obs      | Calc |
| N(1)  | 445      | 446  | 527      | 538  | 441      | 382  | -6       | -17  | -81      | -46  | -50      | -35  |
| N(2)  | 426      | 527  | 599      | 515  | 508      | 412  | 25       | -11  | -77      | -41  | -17      | -16  |
| N(3)  | 411      | 440  | 597      | 572  | 586      | 452  | 48       | 19   | 26       | -10  | -21      | -20  |
| N(4)  | 424      | 444  | 447      | 515  | 376      | 382  | -1       | -14  | -6       | -35  | -6       | -23  |
| C(1)  | 400      | 441  | 586      | 527  | 370      | 374  | 44       | -16  | -107     | -43  | -31      | -18  |
| C(2)  | 531      | 460  | 528      | 556  | 339      | 394  | -2       | -3   | -60      | -45  | 12       | 6    |
| C(3)  | 493      | 454  | 587      | 628  | 501      | 421  | -11      | 20   | -75      | -51  | 86       | 17   |
| C(4)  | 480      | 489  | 718      | 689  | 457      | 490  | 1        | 50   | -19      | -38  | 24       | 71   |
| C(5)  | 640      | 562  | 606      | 653  | 559      | 535  | 81       | 44   | 22       | -19  | 72       | 107  |
| C(6)  | 634      | 580  | 612      | 572  | 452      | 493  | 3        | 12   | -40      | -24  | -1       | 67   |
| C(7)  | 448      | 512  | 571      | 538  | 370      | 421  | -10      | -4   | -2       | -38  | 36       | 19   |
| C(8)  | 553      | 480  | 552      | 518  | 407      | 392  | -37      | -9   | -50      | -41  | 6        | -34  |
| C(9)  | 500      | 490  | 551      | 553  | 350      | 416  | -24      | 9    | -33      | -43  | -62      | -66  |
| C(10) | 607      | 563  | 581      | 575  | 476      | 446  | 70       | 18   | -62      | -57  | -77      | -108 |
| C(11) | 588      | 578  | 610      | 657  | 501      | 486  | 43       | 55   | -47      | -68  | -172     | -163 |
| C(12) | 462      | 511  | 788      | 729  | 459      | 515  | 47       | 90   | -96      | -55  | -139     | -146 |
| C(13) | 413      | 460  | 645      | 687  | 536      | 503  | 114      | 74   | -77      | -29  | -66      | -81  |
| C(14) | 437      | 454  | 546      | 594  | 385      | 445  | -7       | 30   | -5       | -29  | -122     | -56  |
| C(15) | 435      | 441  | 526      | 528  | 463      | 415  | 11       | -5   | 41       | -19  | 27       | -18  |
| C(16) | 509      | 467  | 507      | 519  | 349      | 440  | 21       | -13  | -16      | -8   | -64      | -11  |
| C(17) | 459      | 512  | 512      | 539  | 490      | 526  | -106     | 0    | 94       | 24   | 61       | 19   |
| C(18) | 580      | 591  | 518      | 526  | 608      | 584  | 49       | -8   | 11       | 36   | 24       | 19   |
| C(19) | 721      | 606  | 525      | 515  | 556      | 540  | -27      | -25  | -8       | 5    | -32      | -32  |
| C(20) | 468      | 534  | 573      | 527  | 481      | 456  | -15      | -26  | -24      | -27  | -92      | -56  |
| C(21) | 450      | 473  | 475      | 519  | 313      | 414  | -66      | -23  | -43      | -28  | 69       | -34  |

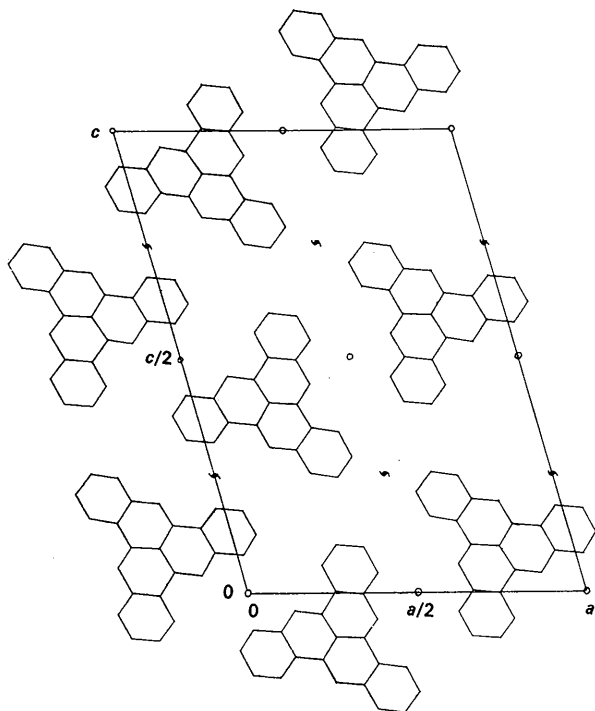


Fig. 6. Packing arrangement of molecules projected on (010).

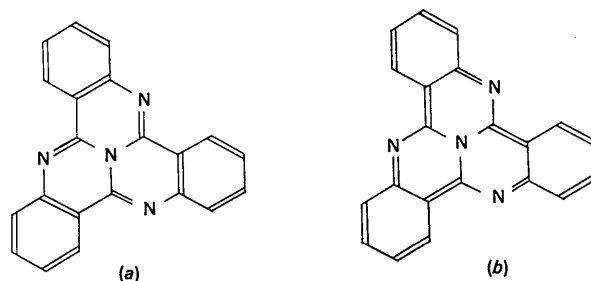


Fig. 7. The two arrangements of double bonds in central rings for covalent Kekulé structures.

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## The Crystal Structure of a Benzocyclopropapyran\*

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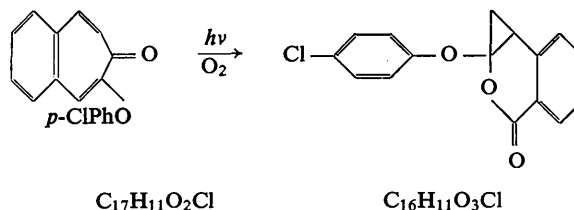
Crystals of 1*a*-(*p*-chlorophenoxy)-1*a*,7*b*-dihydrobenzo[*d*]cyclopropa[*b*]pyran-3(1*H*)one, C<sub>16</sub>H<sub>11</sub>O<sub>3</sub>Cl, belong to the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub> with four molecules in a unit cell of dimensions *a* = 13.21, *b* = 13.80, and *c* = 7.33, all ± 0.01 Å. The crystal structure was determined by a three-dimensional X-ray analysis of counter data using weighted Patterson superposition techniques and was refined by least-squares methods to a conventional *R* index of 6.9%. The combined benzene and lactone rings are nearly planar and the dihedral angles between this plane and the phenoxy group and cyclopropane ring are 64 and 70°, respectively.

### Introduction

One of the photolysis products found by Stoner (1964) on the irradiation of 2-(*p*-chlorophenoxy)-4,5-benzotropone is 1*a*-(*p*-chlorophenoxy)-1*a*,7*b*-dihydrobenzo[*d*]cyclopropa[*b*]pyran-3(1*H*)one, C<sub>16</sub>H<sub>11</sub>O<sub>3</sub>Cl.

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Elemental analysis indicated the loss of one carbon atom and addition of one oxygen atom; this, along with