

Tableau 1. Coordonnées atomiques et facteurs d'agitation thermique isotrope équivalents (Å<sup>2</sup>)
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

|     | x          | y           | z           | B <sub>eq</sub> |
|-----|------------|-------------|-------------|-----------------|
| C1  | 0,6779 (3) | -0,0679 (4) | 0,2321 (3)  | 4,5 (1)         |
| C2  | 0,6905 (4) | -0,1935 (5) | 0,2777 (3)  | 5,4 (1)         |
| C3  | 0,6030 (4) | -0,2848 (4) | 0,3517 (3)  | 5,0 (1)         |
| C4  | 0,4999 (3) | -0,2550 (4) | 0,3805 (3)  | 4,6 (1)         |
| C5  | 0,4888 (3) | -0,1292 (4) | 0,3332 (3)  | 4,3 (1)         |
| C6  | 0,5766 (3) | -0,0332 (4) | 0,2595 (2)  | 3,8 (1)         |
| C7  | 0,5674 (3) | 0,0985 (4)  | 0,2074 (3)  | 4,2 (1)         |
| C8  | 0,6609 (3) | 0,1971 (4)  | 0,1439 (2)  | 3,9 (1)         |
| C9  | 0,7778 (4) | 0,1693 (5)  | 0,1254 (3)  | 5,5 (1)         |
| O10 | 0,7592 (3) | 0,0109 (4)  | 0,1533 (2)  | 6,9 (1)         |
| C11 | 0,4017 (4) | -0,3612 (5) | 0,4577 (3)  | 6,4 (1)         |
| C12 | 0,6557 (3) | 0,3311 (4)  | 0,0935 (3)  | 4,3 (1)         |
| C13 | 0,7426 (3) | 0,4355 (4)  | 0,0267 (3)  | 4,5 (1)         |
| C14 | 0,7311 (3) | 0,5666 (4)  | -0,0192 (3) | 4,4 (1)         |
| C15 | 0,8160 (3) | 0,6710 (4)  | -0,0864 (3) | 4,7 (1)         |
| C16 | 0,8036 (3) | 0,8023 (4)  | -0,1328 (3) | 4,5 (1)         |
| C17 | 0,8854 (3) | 0,9056 (4)  | -0,2003 (3) | 4,6 (1)         |
| C18 | 0,8648 (3) | 1,0335 (4)  | -0,2459 (3) | 4,4 (1)         |
| O19 | 0,9461 (2) | 1,1049 (3)  | -0,3235 (2) | 4,7 (1)         |
| C20 | 0,9299 (4) | 1,2268 (4)  | -0,3811 (3) | 5,2 (1)         |
| C21 | 1,0436 (4) | 1,3029 (5)  | -0,4520 (3) | 6,1 (1)         |
| O22 | 0,7871 (3) | 1,0781 (4)  | -0,2173 (3) | 7,4 (1)         |

Tableau 2. Paramètres géométriques (Å, °)

|           |           |             |           |
|-----------|-----------|-------------|-----------|
| C1—C2     | 1,380 (7) | C9—O10      | 1,404 (6) |
| C1—C6     | 1,402 (6) | C12—C13     | 1,348 (6) |
| C1—O10    | 1,359 (6) | C13—C14     | 1,422 (6) |
| C2—C3     | 1,378 (7) | C14—C15     | 1,343 (6) |
| C3—C4     | 1,399 (6) | C15—C16     | 1,431 (6) |
| C4—C5     | 1,383 (6) | C16—C17     | 1,328 (6) |
| C4—C11    | 1,503 (7) | C17—C18     | 1,448 (6) |
| C5—C6     | 1,389 (6) | C18—O19     | 1,333 (5) |
| C6—C7     | 1,450 (6) | C18—O22     | 1,209 (6) |
| C7—C8     | 1,335 (6) | O19—C20     | 1,442 (6) |
| C8—C9     | 1,507 (6) | C20—C21     | 1,497 (7) |
| C8—C12    | 1,438 (6) |             |           |
| C2—C1—C6  | 120,8 (4) | C9—C8—C12   | 118,5 (4) |
| C2—C1—O10 | 117,9 (4) | C8—C9—O10   | 116,4 (4) |
| C6—C1—O10 | 121,2 (4) | C1—O10—C9   | 120,8 (4) |
| C1—C2—C3  | 119,5 (4) | C8—C12—C13  | 127,4 (4) |
| C2—C3—C4  | 121,5 (4) | C12—C13—C14 | 123,9 (4) |
| C3—C4—C5  | 118,0 (4) | C13—C14—C15 | 124,8 (4) |
| C3—C4—C11 | 120,6 (4) | C14—C15—C16 | 124,6 (4) |
| C5—C4—C11 | 121,4 (4) | C15—C16—C17 | 125,6 (4) |
| C4—C5—C6  | 122,0 (4) | C16—C17—C18 | 122,5 (4) |
| C1—C6—C5  | 118,3 (4) | C17—C18—O19 | 112,1 (4) |
| C1—C6—C7  | 118,1 (4) | C17—C18—O22 | 126,0 (4) |
| C5—C6—C7  | 123,6 (4) | O19—C18—O22 | 121,8 (4) |
| C6—C7—C8  | 121,5 (4) | C18—O19—C20 | 117,8 (3) |
| C7—C8—C9  | 119,0 (4) | O19—C20—C21 | 107,1 (4) |
| C7—C8—C12 | 122,5 (4) |             |           |

Collection des données: CAD-4 Software (Enraf-Nonius, 1989). Affinement des paramètres de la maille: CAD-4 Software. Programme(s) pour la solution de la structure: MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71681: 21 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: PA1072]

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### 5-Nitropyrimidines from 3,3-Diamino(2-nitro)thioacrylamides. Structure of 6-(2-Furfurylamino)-2-(2-furyl)-4-methylthio-5-nitropyrimidine

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## Abstract

The single-crystal X-ray structure determination of the product obtained from the methylation of 3,3-bis(2-furfurylamino)-*N*-(2-furoyl)(2-nitro)thioacrylamide, C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>S, shows that the 4-methylthio-substituted 5-nitropyrimidine derivative was obtained, not the 1-methyl-4-thioxo-substituted derivative as previously reported.

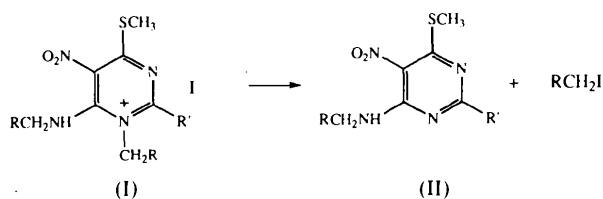
## Comment

The biological importance of nitro-heterocycles is well known. Specifically, some 5-nitropyrimidine derivatives have been reported to show antimetabolic activity (Jamouille *et al.*, 1980) or to be useful as fungicides (Lobov, Stopkan, Cherepenko & Cherkasov, 1965). 5-Nitropyrimidin-2-amine (Enheptin-P) has been used as an effective drug in the therapy of a common protozoan infection in turkeys, known as enterohepatitis (Waletzky, Clark

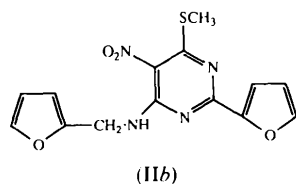
& Marson, 1950). 2,4-Diamino-6-(*p*-bromoanilino)-5-nitropyrimidine is active against the Walker 256 tumour in rats (O'Brien, Cheng & Pfeleiderer, 1966), 5-nitropyrimidine-4,6-diol inhibits the growth of the SSK sarcoma in rats (Grekh, 1965) and 2,4-diamino-6-methyl-5-nitropyrimidine retards the growth of the Crocker sarcoma in mice at 50 mg kg<sup>-1</sup> (Aksamitnaya, 1963).

Recently, we described the synthesis of new 5-nitropyrimidine derivatives, starting from *N*-acyl-3,3-diamino(2-nitro)thioacrylamides and proceeding *via* *S*-methyl *N*-acyl-3,3-diamino(2-nitro)thioacrylimide hydroiodides (García Trimiño, Macías Cabrera & Vélez Castro, 1992). Based on the available spectroscopic data (IR, <sup>1</sup>H NMR and MS) and consideration of the likely mechanism of the reaction, it was proposed that the thioimide salts cyclize upon heating to 6-amino-4-methylthio-5-nitropyrimidinium iodides (I), which finally transform to the 6-amino-5-nitro-4-thioxopyrimidines.

Subsequently, studies by <sup>13</sup>C NMR and the X-ray structure determinations of two of the derivatives have shown that the 6-amino-4-methylthio-5-nitropyrimidines (II) were the actual products. The X-ray structure of 6-methylamino-4-methylthio-5-nitro-2-phenylpyrimidine [(IIa), *R* = H, *R'* = Ph] has been determined by Pomes,



Duque, Nova & García Trimiño (1994). In the present work, the structure of 6-(2-furfurylamino)-2-(2-furyl)-4-methylthio-5-nitropyrimidine [(IIb), *R* = 2-furyl, *R'* = 2-furyl] is reported.



These later findings suggest that in (I) the nucleophilic attack by the iodide anion occurs at the C atom attached to N(1) of the pyrimidine ring, instead of, as originally proposed, at the C atom of the —SCH<sub>3</sub> group. Such an attack can be explained by the increased electrophilicity of the C atom attached to the positively charged N(1) atom of the pyrimidinium salt. Similar behaviour has been described previously in the case of 1-substituted 4-methylthio-pyridinium salts (Spitzner, Lesinski, Richter & Schroth, 1987).

A view of a molecule of (IIb) is shown in Fig. 1. The structure does not exhibit any unusual features. There is an intramolecular hydrogen bond between the amine H atom and the nearest O atom of the nitro group. The contact distance H(6)···O(2) is 1.89 (3) Å. The pyrimidine ring and the 2-(2-furyl) substituent are coplanar, which indicates an extension of the delocalized π-bonding system across both rings. A least-squares-planes calculation involving the atoms of both rings plus the atoms S, N(5) and N(6) showed that the maximum deviation from planarity was 0.05 Å at N(5).

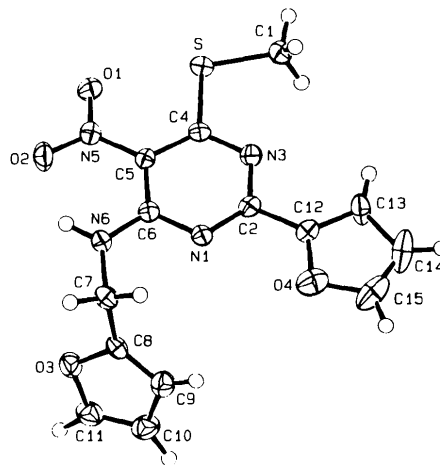


Fig. 1. View of a molecule of (IIb) showing the atom-labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

## Experimental

6-(2-Furfurylamino)-2-(2-furyl)-4-methylthio-5-nitropyrimidine was obtained in 65% yield by methylation of 3,3-bis(2-furfurylamino)-*N*-(2-furoyl)(2-nitro)thioacrylamide with CH<sub>3</sub>I in ethanol (García Trimiño, Macías Cabrera & Vélez Castro, 1992). Recrystallization from acetone gave light yellow needles (m.p. 432–434 K).

### Crystal data

C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>S

*M<sub>r</sub>* = 332.33

Triclinic

*P* $\bar{1}$

*a* = 11.099 (3) Å

*b* = 15.200 (4) Å

*c* = 4.416 (2) Å

$\alpha$  = 95.23 (3)°

$\beta$  = 96.84 (3)°

$\gamma$  = 93.74 (2)°

*V* = 734.5 (4) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.503 Mg m<sup>-3</sup>

Mo *K*α radiation

$\lambda$  = 0.71069 Å

Cell parameters from 24

reflections

$\theta$  = 15–20°

$\mu$  = 0.235 mm<sup>-1</sup>

*T* = 173 (1) K

Needle

0.43 × 0.10 × 0.05 mm

Yellow

### Data collection

Rigaku AFC-5R diffractometer

*R*<sub>int</sub> = 0.033

$\theta_{\text{max}}$  = 27.5°

$\omega/2\theta$  scans  
Absorption correction:  
empirical (DIFABS:  
Walker & Stuart, 1983)  
 $T_{\min} = 0.86$ ,  $T_{\max} = 1.19$   
3546 measured reflections  
3374 independent reflections  
2134 observed reflections  
 $|I| > 3\sigma(I)$

$h = 0 \rightarrow 14$   
 $k = -19 \rightarrow 19$   
 $l = -5 \rightarrow 5$   
3 standard reflections  
monitored every 150  
reflections  
intensity variation:  
insignificant

### Refinement

Refinement on  $F$   
 $R = 0.0456$   
 $wR = 0.0427$   
 $S = 1.640$   
2134 reflections  
254 parameters  
H atoms refined isotropically  
 $w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$   
 $(\Delta/\sigma)_{\max} = 0.0005$

$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$   
Extinction correction:  
Zachariasen (1963)  
Extinction coefficient:  
 $2(2) \times 10^{-7}$   
Atomic scattering factors  
from *International Tables*  
for X-ray Crystallography  
(1974, Vol. 4)

|                 |           |                   |           |
|-----------------|-----------|-------------------|-----------|
| C(2)—N(1)—C(6)  | 116.7 (3) | N(6)—C(6)—C(5)    | 124.0 (3) |
| C(2)—N(3)—C(4)  | 116.7 (3) | N(6)—C(7)—C(8)    | 113.9 (3) |
| O(1)—N(5)—O(2)  | 121.4 (3) | O(3)—C(8)—C(7)    | 116.6 (3) |
| O(1)—N(5)—C(5)  | 119.1 (3) | O(3)—C(8)—C(9)    | 109.3 (3) |
| O(2)—N(5)—C(5)  | 119.5 (3) | C(7)—C(8)—C(9)    | 134.0 (3) |
| C(6)—N(6)—C(7)  | 122.5 (3) | C(8)—C(9)—C(10)   | 107.8 (3) |
| N(1)—C(2)—N(3)  | 127.6 (3) | C(9)—C(10)—C(11)  | 106.0 (3) |
| N(1)—C(2)—C(12) | 117.8 (3) | O(3)—C(11)—C(10)  | 110.6 (3) |
| N(3)—C(2)—C(12) | 114.6 (3) | O(4)—C(12)—C(2)   | 120.5 (3) |
| S—C(4)—N(3)     | 116.3 (2) | O(4)—C(12)—C(13)  | 111.8 (3) |
| S—C(4)—C(5)     | 122.4 (2) | C(2)—C(12)—C(13)  | 127.7 (3) |
| N(3)—C(4)—C(5)  | 121.3 (3) | C(12)—C(13)—C(14) | 105.0 (3) |
| N(5)—C(5)—C(4)  | 120.7 (3) | C(13)—C(14)—C(15) | 108.2 (4) |
| N(5)—C(5)—C(6)  | 121.9 (3) | O(4)—C(15)—C(14)  | 110.1 (4) |

The H atoms were located from a difference electron density map and refined isotropically, except H(13) for which the position was calculated and only  $U_{\text{iso}}$  refined. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

|       | $x$         | $y$         | $z$        | $U_{\text{eq}}$ |
|-------|-------------|-------------|------------|-----------------|
| S     | 0.92094 (7) | 0.92811 (5) | 1.2329 (2) | 0.0256 (2)      |
| O(1)  | 1.0883 (2)  | 0.8169 (2)  | 1.2209 (5) | 0.0358 (8)      |
| O(2)  | 1.1074 (2)  | 0.7036 (2)  | 0.8978 (5) | 0.0397 (8)      |
| O(3)  | 0.8290 (2)  | 0.4531 (1)  | 0.5065 (5) | 0.0326 (8)      |
| O(4)  | 0.5294 (2)  | 0.7487 (2)  | 0.1884 (6) | 0.0477 (9)      |
| N(1)  | 0.7618 (2)  | 0.7246 (2)  | 0.4556 (5) | 0.0235 (8)      |
| N(3)  | 0.7527 (2)  | 0.8566 (2)  | 0.7966 (6) | 0.0250 (8)      |
| N(5)  | 1.0478 (2)  | 0.7652 (2)  | 0.9927 (6) | 0.0273 (9)      |
| N(6)  | 0.9292 (2)  | 0.6447 (2)  | 0.4713 (6) | 0.0264 (9)      |
| C(1)  | 0.8026 (3)  | 1.0032 (2)  | 1.2092 (9) | 0.034 (1)       |
| C(2)  | 0.7075 (3)  | 0.7945 (2)  | 0.5652 (7) | 0.0233 (9)      |
| C(4)  | 0.8630 (3)  | 0.8470 (2)  | 0.9349 (6) | 0.0214 (9)      |
| C(5)  | 0.9302 (3)  | 0.7749 (2)  | 0.8418 (7) | 0.0212 (9)      |
| C(6)  | 0.8752 (3)  | 0.7144 (2)  | 0.5895 (7) | 0.0234 (9)      |
| C(7)  | 0.8665 (3)  | 0.5803 (2)  | 0.2254 (7) | 0.027 (1)       |
| C(8)  | 0.7797 (3)  | 0.5153 (2)  | 0.3310 (7) | 0.0249 (9)      |
| C(9)  | 0.6585 (3)  | 0.5006 (2)  | 0.2880 (8) | 0.037 (1)       |
| C(10) | 0.6275 (3)  | 0.4248 (2)  | 0.4381 (9) | 0.040 (1)       |
| C(11) | 0.7329 (3)  | 0.3988 (2)  | 0.5669 (9) | 0.038 (1)       |
| C(12) | 0.5861 (3)  | 0.8074 (2)  | 0.4235 (7) | 0.027 (1)       |
| C(13) | 0.5153 (3)  | 0.8723 (2)  | 0.4972 (8) | 0.037 (1)       |
| C(14) | 0.4042 (4)  | 0.8520 (4)  | 0.298 (1)  | 0.061 (2)       |
| C(15) | 0.4157 (4)  | 0.7800 (3)  | 0.116 (1)  | 0.056 (2)       |

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                  |           |                |           |
|------------------|-----------|----------------|-----------|
| S—C(1)           | 1.796 (4) | N(6)—C(6)      | 1.346 (4) |
| S—C(4)           | 1.751 (3) | N(6)—C(7)      | 1.469 (4) |
| O(1)—N(5)        | 1.240 (3) | C(2)—C(12)     | 1.450 (4) |
| O(2)—N(5)        | 1.251 (3) | C(4)—C(5)      | 1.422 (4) |
| O(3)—C(8)        | 1.377 (3) | C(5)—C(6)      | 1.428 (4) |
| O(3)—C(11)       | 1.371 (4) | C(7)—C(8)      | 1.479 (4) |
| O(4)—C(12)       | 1.368 (4) | C(8)—C(9)      | 1.337 (4) |
| O(4)—C(15)       | 1.389 (5) | C(9)—C(10)     | 1.424 (5) |
| N(1)—C(2)        | 1.336 (4) | C(10)—C(11)    | 1.339 (5) |
| N(1)—C(6)        | 1.350 (4) | C(12)—C(13)    | 1.341 (4) |
| N(3)—C(2)        | 1.353 (4) | C(13)—C(14)    | 1.426 (5) |
| N(3)—C(4)        | 1.325 (4) | C(14)—C(15)    | 1.319 (6) |
| N(5)—C(5)        | 1.417 (4) |                |           |
| C(1)—S—C(4)      | 100.5 (2) | C(4)—C(5)—C(6) | 117.4 (3) |
| C(8)—O(3)—C(11)  | 106.3 (3) | N(1)—C(6)—N(6) | 115.7 (3) |
| C(12)—O(4)—C(15) | 104.9 (3) | N(1)—C(6)—C(5) | 120.3 (3) |

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71560 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1074]

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## Structure of a Cyclopropachromene

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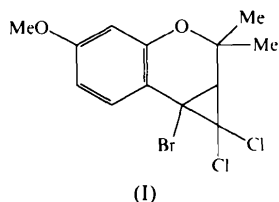
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### Abstract

The tricyclic molecule 3a-bromo-3,3-dichloro-2a,3a-dihydro-6-methoxy-2,2-dimethyl-2*H*,3*H*-cyclopropa[2,3-*c*]chromene, C<sub>13</sub>H<sub>13</sub>BrCl<sub>2</sub>O<sub>2</sub>, has a pyran ring fused to both a benzene ring and a cyclopropane ring, constraining the degree of puckering so that only two C atoms lie markedly out of the mean plane of the other atoms. The cyclopropane ring is positioned pseudo-axially relative to the pyran ring.

### Comment

The title compound (I) was prepared in order to compare its ease of Ag-ion-assisted solvolysis with that of the corresponding trichloro compound (which has a Cl in place of the Br atom). The comparison of the two reactions served to demonstrate the probable mechanism of solvolysis (Brown & Islam, 1987; Brown, Clegg, Islam & Steele, 1990).



Although the chroman and chromene ring systems are constituents of the molecules of many natural products and pharmaceutical substances, whose crystal structures have been reported widely, cyclopropa[*c*]chromene derivatives have not been documented previously.

The conformation of the pyran ring is constrained by the fused benzene and cyclopropane rings, imposing small ring torsion angles about the C4a—C8a and C3—C4 bonds (−3.3 and −6.7°, respectively). Thus, with reference to the mean plane of the atoms O1, C8a, C4a and

C4 (r.m.s.  $\Delta = 0.010$  Å), C3 lies only 0.246 Å out of the plane, compared with 0.602 Å for C2. The cyclopropane ring is positioned pseudo-axially, with the Br atom and the H atom attached to C3 occupying pseudo-equatorial sites on the pyran ring (Fig. 1).

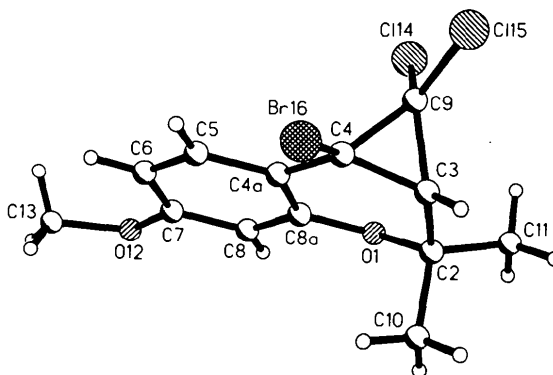


Fig. 1. Molecular structure of the cyclopropachromene illustrating the ring conformations.

The C atom of the methoxy substituent lies almost in the plane of the benzene ring, allowing some involvement of oxygen in the delocalized  $\pi$ -bonding system. There are no unusual intramolecular or intermolecular interactions.

### Experimental

The compound was prepared as described previously (Brown, Clegg, Islam & Steele, 1990) and crystallized from light petroleum.

#### Crystal data

C<sub>13</sub>H<sub>13</sub>BrCl<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 352.04  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 12.434 (2) Å  
*b* = 10.244 (2) Å  
*c* = 11.134 (2) Å  
 $\beta$  = 100.851 (14)°  
*V* = 1392.8 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.679 Mg m<sup>−3</sup>

Cu *K* $\alpha$  radiation  
 $\lambda$  = 1.5418 Å  
 Cell parameters from 32 reflections  
 $\theta$  = 24.14–27.68°  
 $\mu$  = 7.486 mm<sup>−1</sup>  
*T* = 295 (2) K  
 Block  
 0.56 × 0.48 × 0.44 mm  
 Colourless

#### Data collection

Stoe Siemens diffractometer  
 $\omega/\theta$  scans with on-line profile fitting (Clegg, 1981)  
 Absorption correction: empirical  
 $T_{\min}$  = 0.016,  $T_{\max}$  = 0.107  
 9281 measured reflections  
 2336 independent reflections  
 2224 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

$R_{\text{int}}$  = 0.0774  
 $\theta_{\text{max}}$  = 64.99°  
*h* = −14 → 14  
*k* = −12 → 12  
*l* = −12 → 12  
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 3%