

The plane of the C(2) methoxy group is inclined at 24.4° to the plane of the phenyl ring, presumably an effect of crystal packing forces, whereas the C(6) methoxy group makes an angle of only 2.8° with the phenyl plane.

The molecules have an unusual hydrogen-bonding scheme, being linked through the carboxy groups into infinite, interlocking ribbons extending parallel to **b**. A view of the molecular packing, seen in *a*-axis projection, is given in Fig. 2.

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trans-syn Cyclobutane-Type Photodimers of 1,3,3-Trimethyl-2,4(1*H*,3*H*)-pyridinedione and 1,3,3,6-Tetramethyl-2,4(1*H*,3*H*)-pyridinedione

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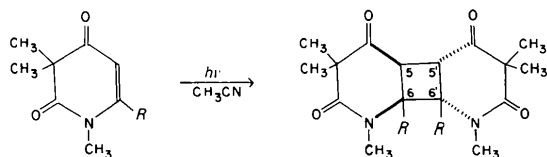
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Abstract. (I) $C_{16}H_{22}N_2O_4$, monoclinic, $P2_1/c$, $a = 6.370$ (2), $b = 13.989$ (9), $c = 17.598$ (6) Å, $\beta = 100.56$ (2)°, $Z = 4$, $M_r = 306.4$, $V = 1541.6$ Å³, $D_x = 1.320$ g cm⁻³, $R = 5.9\%$ for 1901 observed reflections. (II) $C_{18}H_{26}N_2O_4$, monoclinic, $P2_1/a$, $a = 12.245$ (4), $b = 11.929$ (3), $c = 12.467$ (3) Å, $\beta = 108.92$ (2)°, $Z = 4$, $M_r = 334.4$, $V = 1722.7$ Å³, $D_x = 1.289$ g cm⁻³, $R = 7.4\%$ for 2180 observed reflections. Methylated analogues of uracil in which N(3) has been replaced by a tetrahedral C atom undergo photodimerization to form cyclobutane-type dimers. Unlike the pyrimidines, the most prevalent irradiation products of these pyridine analogues are the *trans-syn* dimers. Bond lengths and angles are very similar in the two dimers, except for the C(6)–C(6') bond which is considerably longer in the dimer with methyl substituents on C(6) and C(6').

Introduction. Irradiation of pyrimidines can produce cyclobutane-type dimers, formed by opening of the double bond at the C(5)–C(6) position. Four different types of dimers can be formed and each type has been characterized by crystal-structure analyses (Karle, 1976, and references therein). The *cis-syn* dimer is the most prevalent product both from irradiated DNA and from the irradiation of frozen thymine or uracil

solutions. The dimer of methyl orotate had been the only example of a crystal-structure analysis of a *trans-syn* dimer (Birnbbaum, 1972). Methyl orotate is resistant to dimerization in the frozen state but dimerizes efficiently in solution (Fisher & Johns, 1976).

In the present paper it is shown that the principal irradiation products of methylated analogues of uracil, in which N(3) has been replaced by a tetrahedral C atom, are the *trans-syn* cyclobutane-type dimers (compounds I and II):



(I) $R = H$, m.p. 488–489 K

(II) $R = CH_3$, m.p. 528 K

Crystals of dimers (I) and (II) were supplied by Y. Kanaoka, Hokkaido University (Kanaoka, Hasebe & Sato, 1980; Hasebe, 1980).

Diffraction data were collected from clear, colorless prisms of (I) and (II), grown from ethyl acetate, on a Nicolet P3F diffractometer equipped with a graphite monochromator. The $\theta/2\theta$ scanning mode was used

Table 1. Fractional coordinates and B_{eq} values for the *trans-syn* photodimer of 1,3,3-trimethyl-2,4(1*H*,3*H*)-pyridinedione

The e.s.d.'s for x , y and z are 0.0005, 0.0002 and 0.0002 respectively. The e.s.d.'s for B_{eq} are less than 0.1 Å². $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$

| | x | y | z | B_{eq} (Å ²) |
|-------|---------|--------|--------|----------------------------|
| N(1) | 0.0072 | 0.8063 | 0.2300 | 2.6 |
| C(2) | -0.1443 | 0.8261 | 0.1674 | 3.0 |
| O(2) | -0.3274 | 0.7945 | 0.1606 | 4.2 |
| C(3) | -0.0805 | 0.8873 | 0.1020 | 2.8 |
| C(4) | 0.0782 | 0.9624 | 0.1376 | 2.7 |
| O(4) | 0.0571 | 1.0470 | 0.1231 | 3.7 |
| C(5) | 0.2683 | 0.9252 | 0.1924 | 2.5 |
| C(6) | 0.2312 | 0.8357 | 0.2401 | 2.5 |
| C(7) | -0.0408 | 0.7357 | 0.2866 | 3.7 |
| C(8) | -0.2794 | 0.9327 | 0.0531 | 4.1 |
| C(9) | 0.0329 | 0.8205 | 0.0514 | 3.6 |
| N(1') | 0.5050 | 0.8593 | 0.3642 | 3.0 |
| C(2') | 0.6766 | 0.9155 | 0.3919 | 3.1 |
| O(2') | 0.8325 | 0.8845 | 0.4357 | 4.7 |
| C(3') | 0.6663 | 1.0213 | 0.3664 | 2.7 |
| C(4') | 0.5573 | 1.0247 | 0.2822 | 3.1 |
| O(4') | 0.6375 | 1.0567 | 0.2307 | 5.7 |
| C(5') | 0.3341 | 0.9831 | 0.2675 | 2.6 |
| C(6') | 0.3082 | 0.8938 | 0.3170 | 2.6 |
| C(7') | 0.4973 | 0.7629 | 0.3975 | 4.4 |
| C(8') | 0.8922 | 1.0639 | 0.3760 | 4.2 |
| C(9') | 0.5340 | 1.0781 | 0.4168 | 3.7 |

Table 2. Fractional coordinates and B_{eq} values for the *trans-syn* photodimer of 1,3,3,6-tetramethyl-2,4(1*H*,3*H*)-pyridinedione

The e.s.d.'s for x , y and z are 0.0004. The e.s.d.'s for B_{eq} are less than 0.1 Å². $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$

| | x | y | z | B_{eq} (Å ²) |
|--------|--------|--------|--------|----------------------------|
| N(1) | 0.4130 | 0.6866 | 0.1849 | 3.5 |
| C(2) | 0.4144 | 0.7951 | 0.2146 | 3.7 |
| O(2) | 0.4475 | 0.8689 | 0.1645 | 4.8 |
| C(3) | 0.3714 | 0.8291 | 0.3136 | 3.9 |
| C(4) | 0.2833 | 0.7444 | 0.3216 | 3.5 |
| O(4) | 0.1869 | 0.7711 | 0.3200 | 4.8 |
| C(5) | 0.3208 | 0.6256 | 0.3307 | 3.3 |
| C(6) | 0.3815 | 0.5916 | 0.2431 | 3.3 |
| C(7) | 0.4621 | 0.6614 | 0.0943 | 5.0 |
| C(8) | 0.4777 | 0.8247 | 0.4236 | 5.2 |
| C(9) | 0.3211 | 0.9468 | 0.2958 | 5.6 |
| C(10) | 0.4844 | 0.5140 | 0.2975 | 4.4 |
| N(1') | 0.2788 | 0.4102 | 0.1442 | 3.6 |
| C(2') | 0.2471 | 0.3172 | 0.1879 | 3.9 |
| O(2') | 0.2561 | 0.2238 | 0.1530 | 5.9 |
| C(3') | 0.1912 | 0.3302 | 0.2820 | 3.7 |
| C(4') | 0.2352 | 0.4350 | 0.3495 | 3.8 |
| O(4') | 0.2733 | 0.4349 | 0.4516 | 6.5 |
| C(5') | 0.2260 | 0.5384 | 0.2810 | 3.3 |
| C(6') | 0.2652 | 0.5252 | 0.1743 | 3.1 |
| C(7') | 0.3207 | 0.3904 | 0.0474 | 5.3 |
| C(8') | 0.0573 | 0.3428 | 0.2208 | 5.6 |
| C(9') | 0.2159 | 0.2267 | 0.3576 | 5.6 |
| C(10') | 0.1871 | 0.5902 | 0.0733 | 4.3 |

with variable scanning speed dependent upon the magnitude of the intensity and data were collected to $2\theta_{max} = 112^\circ$ with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). Three reflections used as standards were measured after intervals of 50 measurements. Their intensities remained constant during the data collection. The data were corrected for Lorentz and polarization effects but not for absorption.

Each structure was solved by direct phase determination using the symbolic addition procedure. The positions of most of the H atoms were derived from difference maps. For several H atoms in (II), idealized positions were used.

Both structures were refined on all the data by anisotropic full-matrix least-squares refinement on the heavy atoms while the approximate parameters for the H atoms were kept constant. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weighting based on counting statistics (Gilardi, 1973). For (I), $R = 6.3\%$ for all 2007 data and 5.9% for 1901 intensities $> 1\sigma$, while for (II), $R = 7.6\%$ for all 2253 data and 7.3% for 2180 intensities $> 1\sigma$. Coordinates and B_{eq} values for the non-H atoms are listed in Tables 1 and 2.*

Discussion. Both dimers (I) and (II), shown in Figs. 1 and 2, have the *trans-syn* configuration. Although in each crystal the molecules lie in general positions, an approximate twofold rotation axis that passes near the mid-points of the C(5)–C(5') bond and the C(6)–C(6') bond relates one-half of each molecule to the other half. The averages of the coordinates of pairs of atoms related by the pseudo rotation axis lie within 0.10 and 0.04 Å of the pseudo symmetry axes for dimers (I) and (II) respectively. In many respects, dimers (I) and (II) resemble closely the dimer of methyl

* Lists of structure factors, anisotropic thermal parameters, bond angles and approximate coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36470 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

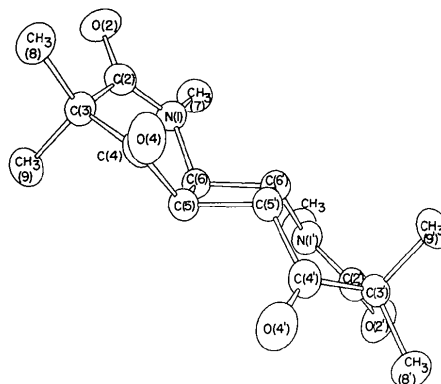


Fig. 1. The *trans-syn* photodimer of 1,3,3-trimethyl-2,4(1*H*,3*H*)-pyridinedione.

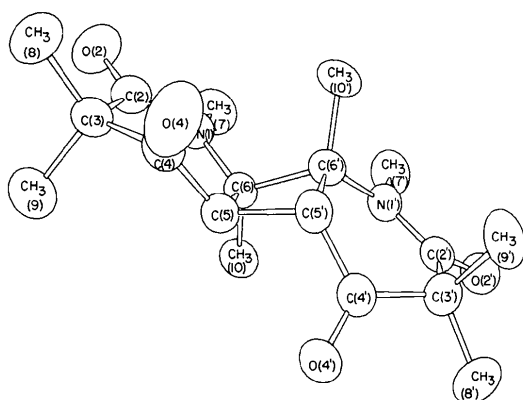


Fig. 2. The *trans-syn* photodimer of 1,3,3,6-tetramethyl-2,4(1*H*,3*H*)-pyridinedione.

Table 3. Bond lengths (Å)

E.s.d.'s are near 0.005 Å for dimer (I) and near 0.007 Å for dimer (II).

| | Dimer (I) | | Dimer (II) | |
|------------|-----------|--------|------------|--------|
| | unprimed | primed | unprimed | primed |
| C(6)–N(1) | 1.464 | 1.453 | 1.463 | 1.446 |
| N(1)–C(2) | 1.353 | 1.363 | 1.345 | 1.348 |
| C(2)–O(2) | 1.233 | 1.220 | 1.222 | 1.214 |
| C(2)–C(3) | 1.548 | 1.545 | 1.544 | 1.546 |
| C(3)–C(4) | 1.512 | 1.519 | 1.505 | 1.505 |
| C(4)–O(4) | 1.212 | 1.205 | 1.216 | 1.205 |
| C(4)–C(5) | 1.497 | 1.514 | 1.483 | 1.483 |
| C(5)–C(6) | 1.547 | 1.550 | 1.561 | 1.562 |
| N(1)–C(7) | 1.475 | 1.475 | 1.473 | 1.475 |
| C(3)–C(8) | 1.532 | 1.538 | 1.555 | 1.576 |
| C(3)–C(9) | 1.557 | 1.549 | 1.521 | 1.522 |
| C(6)–C(10) | | | 1.534 | 1.523 |
| C(5)–C(5') | 1.541 | | 1.533 | |
| C(6)–C(6') | 1.579 | | 1.613 | |

orotate, the only *trans-syn* dimer of a pyrimidine for which structural data are published (Birnbaum, 1972). The latter molecule lies on a true crystallographic twofold axis.

Bond lengths, listed in Table 3, and bond angles are not only quite similar for each half of each dimer but the similarity is maintained between dimers (I) and (II). Furthermore, a very close resemblance of values for the bond lengths and angles exists between the ring systems of these dimers and the dimer of methyl orotate, except, of course, those involving C(3) and C(3'), tetrahedral C atoms that have replaced the planar N(3) and N(3') in the methyl orotate dimer. The C(6)–C(6') bond

Table 4. Torsion angles (°)

E.s.d.'s are near 0.6° for dimer (I) and near 0.8° for dimer (II).

| | Dimer (I) | | Dimer (II) | |
|--------------------|-----------|--------|------------|--------|
| | unprimed | primed | unprimed | primed |
| C(6)N(1)C(2)C(3) | –2 | –5 | –5 | –1 |
| N(1)C(2)C(3)C(4) | –36 | –38 | –28 | –29 |
| C(2)C(3)C(4)C(5) | +53 | +59 | +54 | +52 |
| C(3)C(4)C(5)C(6) | –32 | –38 | –47 | –45 |
| C(4)C(5)C(6)N(1) | –6 | –5 | +13 | +14 |
| C(5)C(6)N(1)C(2) | +24 | +28 | +13 | +10 |
| C(6)C(5)C(5')C(6') | +2 | | –14 | |
| C(5)C(6)C(6')C(5') | +2 | | –13 | |

length needs special mention. The values for this bond are 1.613 and 1.628 Å for dimer (II) and the methyl orotate dimer, as compared to 1.579 Å for dimer (I). The increase in the C(6)–C(6') bond length is correlated with the presence of bulky substituents on C(6) and C(6').

Torsional angles, listed in Table 4, show that the cyclobutyl rings are almost planar. Dihedral angles measuring the fold in the cyclobutyl ring are 177 and 161° for dimers (I) and (II) respectively. The substitution of methyl groups on C(6) and C(6') in dimer (II) causes some minor perturbation in the torsional angles. The six-membered rings can be described as having atoms C(6), N(1), C(2) and C(3) nearly in a plane, and similarly for atoms C(6'), N(1'), C(2') and C(3') while atoms C(4), C(5) and C(4'), C(5') are folded to one side of those planes by 0.88, 0.55 and 0.96, 0.57 Å respectively in dimer (I), and by 0.74, 0.23 and 0.70, 0.22 Å respectively in dimer (II).

There is no possibility for hydrogen bonding and the packing is dominated by van der Waals contacts between methyl groups.

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