There are three examples of cyclic hexapeptides having two *cis* peptide links in the crystalline state; this one, two crystalline forms of *cyclo*-bis(-L-Phe-L-Pro-D-Ala-) and *cyclo*-bis(-L-Phe-L-Pro-D-Gln-). The important feature of the two-*cis* forms is the absence of transannular 4→1 hydrogen bonding. The D-*Yyy* residue in the present structure is in a fully extended conformation whereas in the other two examples it is in a semi-extended conformation with average φ and ψ values of 80 and $-143°$ respectively. The hexapeptide molecule in the present case has an exact twofold symmetry whereas in the other two examples it is only approximate, with differences in values of ψ(Pro) and φ(D-*Yyy*) in the two halves of the molecule.

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Structure of 2,6-Dibromo-*N*-methyl-4-nitroaniline (DBNMNA); a New Electro-Optic Organic Crystal

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Abstract. $C_7H_6Br_2O_2N_2$, $M_r = 309{\cdot}94$, orthorhombic, *Fdd*2, $a = 11{\cdot}745\,(1)$, $b = 29{\cdot}640\,(2)$, $c = 10{\cdot}807\,(2)$ Å, $V = 3762{\cdot}1\,(6)$ Å^3, $Z = 16$, $D_x = 2{\cdot}189$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 108{\cdot}31$ cm^{-1}, $F(000) = 2368$, $T = 296\,(1)$ K, $R = 0{\cdot}043$ based on 714 reflections $[I > 3{\cdot}00\sigma(I)]$ of 799 unique reflections measured, and 117 variables. The DBNMNA molecule has a dihedral angle between the plane of the nitro group and the plane of the ring of 2 (2)° and a dihedral angle between the plane of the *N*-methylamino group and the plane of the ring of 28 (2)°. The 16 molecules of the asymmetric unit pack with all the nitro groups pointing in the same sense, resulting in a polar *c* axis. The net polar orientation was confirmed using second harmonic generation and electro-optic measurements.

Introduction. The high intrinsic optical nonlinearities and low dielectric constants measured for organic crystals (Zyss & Chemla, 1987) have generated sig-

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nificant interest in their use in high-bandwidth electro-optic modulators and switches (Singer, Lalama, Sohn & Small, 1987). We report the crystal structure of DBNMNA, a new nitroaniline-based electro-optic crystal.

Experimental. DBNMNA (m.p. 389–390 K) was prepared by the reaction of bromine with *N*,*N*-dimethyl-4-nitroaniline in methanol at reflux (Tsuda, 1969;* Senear, Rapport, Mead, Maynard & Koepfli, 1946; Blanksma, 1902). Powder X-ray diffraction patterns, obtained using a Philips APD-3600 diffractometer in parafocus geometry using Cu $K\alpha$ radiation, showed that crystals obtained from acetonitrile, ethanol and methylene chloride all have the same structure. The crystal was cut from a rhombohedral platelet obtained from acetonitrile, 0·2 × 0·2 × 0·07 mm. Measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the reflections were monitored with an NaI scintillation counter. Data were collected using the ω–2θ scan technique with scans $(1{\cdot}37 + 0{\cdot}30\tan\theta)^\circ$ at a speed of $32{\cdot}0^\circ\,\text{min}^{-1}$ in ω. Weak reflections $[I < 10{\cdot}0\sigma(I)]$ were rescanned and counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. Cell parameters were measured using 25 reflections, $78{\cdot}07 < 2\theta < 79{\cdot}76^\circ$. The assignment of space group was based on the systematic absences. The linear absorption correction was $108{\cdot}3\,\text{cm}^{-1}$. An empirical absorption correction was applied using the program *DIFABS* (Walker & Stuart, 1983), which resulted in transmission factors of 0·49–1·00. Data were corrected for Lorentz and polarization effects. The maximum value of $\sin(\theta)/\lambda$ was $0{\cdot}5619\,\text{Å}^{-1}$. 799 unique reflections were collected, $0 \le h \le 13$, $0 \le k \le 33$, $0 \le l \le 11$. Intensities of three representative reflections, measured after every 150 reflections, remained constant throughout data collection indicating crystal and electronic stability. The structure was solved using 714 observed reflections $[I > 3{\cdot}00\sigma(I)]$ and the programs *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Non-H atoms were refined anisotropically. Hydrogen atoms were included in the structure-factor calculation in idealized positions ($d_{\text{C—H}} = 0{\cdot}95$ Å) and assigned isotropic thermal parameters which were 20% greater than the B_{eq} value of the atom to which they were bonded. Reflections were given individual weights according to counting statistics and included a factor ($p = 0{\cdot}03$) to downweight intense reflections. Convergence was reached at $R = 0{\cdot}043$, $wR = 0{\cdot}064$, $S = 3{\cdot}09$ with 117 variables. Max. and min. peaks on the final difference Fourier map were 0·44 and $-0{\cdot}51\,\text{e Å}^{-3}$; $\Delta/\sigma = 0{\cdot}0016$. Neutral-atom scattering factors (Cromer & Waber, 1974) and the values of f' and f'' (Cromer, 1974) were taken from *International Tables for X-ray Crystallography*. Anomalous-dispersion effects were included in F_{calc} (Ibers & Hamilton, 1964). All calculations were performed using the *TEXSAN* (Molecular Structure Corporation, 1985) package. Program packages *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976) were also used. Determination of the orientation of the structure with respect to the polar axis was made by refining the model to convergence, switching the signs of the reflection indices and again refining the model to convergence and comparing R factors. The difference in the weighted R factors for the two orientations was only 0·3%. The lowest weighted R-factor refinement is presented. The polar point group assignment was checked by demonstrating efficient second harmonic generation at the fundamental wavelengths of 1·064 and 1·62 μm and also by measuring the electro-optic effect at 0·514, 0·632 and 0·810 μm.

Discussion. Fig. 1 provides an *ORTEP* plot and structural formula for DBNMNA. Atomic coordinates are given in Table 1.* An examination of the measured bond lengths and angles given in Table 2 shows that DBNMNA has a similar structure to that of other nitroanilines. The C(1)—N(1)(nitro) bond length of 1·43 (2) Å and C(4)—N(2)(amino) bond length of 1·37 (2) Å in DBNMNA can be compared with the corresponding bond lengths of 1·440 and 1·406 Å in 3-nitroaniline (Skapsi & Stevenson, 1973), of 1·474 and 1·377 Å in 4-methyl-*N*-methyl-3-nitroaniline (Chiaroni, 1971), of 1·460 and 1·371 Å in 4-nitroaniline (Trueblood, Goldish & Donohue, 1961), of 1·434 and 1·355 Å in 4-nitroaniline (Colapietro, Domenicano, Marciante & Portalone, 1982) and those reported (1·405 and 1·358 Å) for *N*,*N*-dimethyl-4-nitroaniline (Mak & Trotter, 1965). The involvement of quinonoid resonance structures with charge-transfer character should be greater in the 4-nitroanilines than in the 3-position isomers. The observed changes in C—N bond lengths within this series of compounds follows the anticipated trend, though the reported bond-length differences are not greater than 3σ. Since alkylation increases the donor character of the amino group, the extent of contribution of quinonoid structures should be greater in the alkylated nitroanilines and result in shorter C—N bond lengths. DBNMNA, which has a mono-

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* DBNMNA was incorrectly reported as 2,6-dibromo-*N*,*N*-dimethyl-4-nitroaniline.

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53660 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

alkylated amino group, has a C(1)—N(1)(nitro) bond length intermediate between that in 4-nitroaniline and that in *N*,*N*-dimethyl-4-nitroaniline. The benzene ring of DBNMNA does not, however, show a bond alternation pattern indicative of a quinonoid structure. While the C(2)(6)—C(3)(5) bonds are shorter than the C(3)(5)—C(4) bonds, the C(1)—C(2)(6) bonds are just as short as the C(2)(6)—C(3)(5) bonds (Graham, Miskowski, Perry, Coulter, Stiegman, Schaefer & Marsh, 1989). There is a significant steric interaction between the *N*-methylamino group and the ring which may 'mask' or distort the normal bond alternation pattern, see below.

The torsion angles in Table 2 show that the plane of the nitro group is at most 2 (2)° out of the plane of the phenyl ring. However, the torsion angle between the plane of the *N*-methylamino group and that of the ring is 28 (2)°. In 2-methyl-4-nitroaniline (MNA) this angle is only 7·2° (Lipscomb, Garito & Narang, 1981). That the cause of this twist is due primarily to steric interaction between the *N*-methyl group and Br(2) is also indicated by the large C(4)—N(2)—C(7) bond angle of 127 (1)° and the correspondingly smaller C(4)—N(2)—H(1) bond angle of 116·6°. The large C(5)—C(4)—N(2) bond angle of 126 (1)° compared to the C(3)—C(4)—N(2) angle of 120 (1)° is another indication of this steric interaction.

The packing of the 16 DBNMNA molecules in the unit cell (space group *Fdd*2) is shown in the stereographic projection of Fig. 2. The molecules are arranged in four 'rows' of four molecules with all of the nitro groups oriented in the same sense thus producing a polar *c* axis. A vector projected through N(1) and N(2) of each molecule makes an angle θ of ±71·2° with the *c* axis and an angle φ of ±19·4° with the *a* axis. In this respect, DBNMNA is very similar to the electro-optic crystal 3-nitroaniline (*m*NA) which also has *mm*2 point-group symmetry

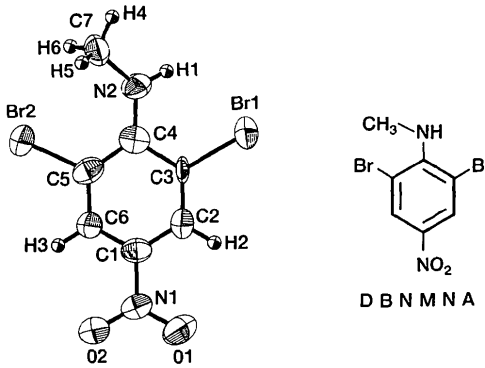

Fig. 1. *ORTEP* plot (50% probability ellipsoids), structural formula and atomic numbering scheme for DBNMNA.

Table 1. *Positional parameters and equivalent isotropic temperature factors, B_{eq} (Å^2), with e.s.d.'s given in parentheses*

	x	*y*	*z*	B_{eq}*
Br(1)	0·8296 (1)	0·18777 (5)	0·0863	5·01 (7)
Br(2)	0·6884 (1)	0·00621 (5)	0·1970 (2)	5·71 (8)
O(1)	0·407 (1)	0·1864 (4)	0·252 (1)	6·4 (6)
O(2)	0·349 (1)	0·1166 (4)	0·270 (1)	6·2 (6)
N(1)	0·426 (1)	0·1448 (4)	0·250 (1)	4·9 (6)
N(2)	0·853 (1)	0·0853 (4)	0·088 (1)	4·5 (5)
C(1)	0·536 (1)	0·1292 (5)	0·213 (1)	3·8 (5)
C(2)	0·617 (1)	0·1596 (4)	0·178 (1)	3·9 (6)
C(3)	0·721 (1)	0·1453 (3)	0·139 (1)	2·9 (4)
C(4)	0·749 (1)	0·0981 (5)	0·132 (1)	3·9 (5)
C(5)	0·662 (1)	0·0686 (5)	0·175 (1)	4·3 (6)
C(6)	0·557 (1)	0·0844 (4)	0·213 (1)	3·7 (5)
C(7)	0·881 (1)	0·0434 (5)	0·028 (1)	5·3 (7)

$*B_{eq} = (8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^* \times \cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

Table 2. *Bond lengths* (Å), *valence and selected torsion angles* (°), *and intermolecular contacts* (Å) *out to* 3·30 Å

Br(1)—C(3)	1·88 (1)	C(1)—C(6)	1·35 (2)
Br(2)—C(5)	1·89 (1)	C(1)—C(2)	1·36 (2)
O(1)—N(1)	1·25 (2)	C(2)—C(3)	1·36 (2)
O(2)—N(1)	1·25 (2)	C(3)—C(4)	1·44 (2)
N(1)—C(1)	1·43 (2)	C(4)—C(5)	1·42 (2)
N(2)—C(4)	1·37 (2)	C(5)—C(6)	1·38 (2)
N(2)—C(7)	1·44 (2)	C(7)—H(5)	0·9
N(2)—H(1)	0·9	C(7)—H(6)	1·0
C(2)—H(2)	1·0	C(7)—H(4)	1·0
C(6)—H(3)	1·0		

O(2)—N(1)—O(1)	122 (1)	C(2)—C(3)—Br(1)	119·7 (8)
O(2)—N(1)—C(1)	119 (1)	C(4)—C(3)—Br(1)	118·8 (9)
O(1)—N(1)—C(1)	119 (1)	N(2)—C(4)—C(5)	126 (1)
C(4)—N(2)—C(7)	127 (1)	N(2)—C(4)—C(3)	120 (1)
C(6)—C(1)—C(2)	121 (1)	C(5)—C(4)—C(3)	115 (1)
C(6)—C(1)—N(1)	119 (1)	C(6)—C(5)—C(4)	122 (1)
C(2)—C(1)—N(1)	120 (1)	C(6)—C(5)—Br(2)	116 (1)
C(1)—C(2)—C(3)	121 (1)	C(4)—C(5)—Br(2)	122 (1)
C(2)—C(3)—C(4)	121 (1)	C(1)—C(6)—C(5)	120 (1)
H(1)—N(2)—C(4)	117	H(5)—C(7)—H(6)	109
H(1)—N(2)—C(7)	116	H(5)—C(7)—H(4)	109
H(2)—C(2)—C(1)	119	H(5)—C(7)—N(2)	110
H(2)—C(2)—C(3)	120	H(6)—C(7)—H(4)	109
H(3)—C(6)—C(1)	119	H(6)—C(7)—N(2)	110
H(3)—C(6)—C(5)	121	H(4)—C(7)—N(2)	109

Br(1)—C(3)—C(2)—C(1)	178 (1)	N(1)—C(1)—C(2)—C(3)	−178 (1)
Br(1)—C(3)—C(4)—N(2)	0 (2)	N(2)—C(4)—C(5)—C(6)	−177 (1)
Br(1)—C(3)—C(4)—C(5)	179·3 (9)	N(2)—C(4)—C(3)—C(2)	177 (1)
Br(2)—C(5)—C(6)—C(1)	173 (1)	C(1)—C(6)—C(5)—C(4)	−2 (2)
Br(2)—C(5)—C(4)—N(2)	9 (2)	C(1)—C(2)—C(3)—C(4)	1 (2)
Br(2)—C(5)—C(4)—C(3)	−170·6 (9)	C(2)—C(1)—C(6)—C(5)	−1 (2)
O(1)—N(1)—C(1)—C(6)	178 (1)	C(2)—C(3)—C(4)—C(5)	−3 (2)
O(1)—N(1)—C(1)—C(2)	−2 (2)	C(3)—C(2)—C(1)—C(6)	2 (2)
O(2)—N(1)—C(1)—C(6)	−6 (2)	C(3)—C(4)—N(2)—C(7)	−153 (1)
O(2)—N(1)—C(1)—C(2)	173 (1)	C(3)—C(4)—C(5)—C(6)	4 (2)
N(1)—C(1)—C(6)—C(5)	179 (1)	C(5)—C(4)—N(2)—C(7)	28 (2)

Atom in mol. at *x*, *y*, *z*	Atom in mol. 2	Distance	ADC*
Br(2)	H(3)	3·1	65502
Br(2)	H(5)	3·2	65510
O(1)	H(4)	2·5	45504
O(1)	H(6)	2·7	65503
O(1)	H(5)	2·9	65503
O(1)	H(1)	3·3	45504
O(1)	C(7)	3·21 (2)	65503
O(2)	H(1)	2·5	45504
O(2)	H(4)	3·1	45504
O(2)	H(4)	3·3	45509
O(2)	H(5)	3·3	45509

Table 2 (*cont.*)

Atom in mol. at *x*, *y*, *z*	Atom in mol. 2	Distance	ADC*
N(1)	H(4)	3·2	45504
N(1)	H(1)	3·3	45504
C(3)	H(1)	3·2	45412
H(6)	H(6)	2·8	75502
H(6)	H(4)	3·0	75502
H(4)	H(3)	2·7	55409
H(4)	H(4)	3·0	75502

* The ADC (atom-designator code) specifies the position of an atom in a crystal. The five-digit number is a composite of three one-digit numbers and one two-digit number: T_a (first digit) + T_b (second digit) + T_c (third digit) + SN (fourth and fifth digits). T_a, T_b and T_c are the crystal-lattice translation digits along cell edges *a*, *b* and *c*. A translation digit of 5 indicates the origin unit cell. If $T_a = 4$, this indicates a translation of one unit-cell length along the *a* axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin ($T_a = 5$, $T_b = 5$, $T_c = 5$) can be represented. The SN or symmetry-operator number refers to the number of the symmetry operator used to generate the coordinates of the target atom. For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell ($T_a = 5$, $T_b = 5$, $T_c = 5$) and its position can be generated using the identity operator (SN = 01). Thus, the ADC for an origin atom is always ADC = 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of that atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through operator 02, then translated -1 cell translations along the *a* axis, $+2$ cell translations along the *b* axis, and 0 cell translations along the *c* axis. An ADC of 1 indicates an intermolecular contact between two fragments (*i.e.* cation and anion) that reside in the same asymmetric unit. Symmetry operators: (01) x, y, z; (02) $-x, -y, z$; (03) $\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z$; (04) $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$; (05) $x, \frac{1}{2}+y, \frac{1}{2}+z$; (06) $-x, \frac{1}{2}-y, \frac{1}{2}+z$; (07) $\frac{1}{4}-x, \frac{3}{4}+y, \frac{3}{4}+z$; (08) $\frac{1}{4}+x, \frac{3}{4}-y, \frac{3}{4}+z$; (09) $\frac{1}{2}+x, y, \frac{1}{2}+z$; (10) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (11) $\frac{3}{4}-x, \frac{1}{4}+y, \frac{3}{4}+z$; (12) $\frac{3}{4}+x, \frac{1}{4}-y, \frac{3}{4}+z$; (13) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (14) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (15) $\frac{3}{4}-x, \frac{3}{4}+y, \frac{1}{4}+z$; (16) $\frac{3}{4}+x, \frac{3}{4}-y, \frac{1}{4}+z$.

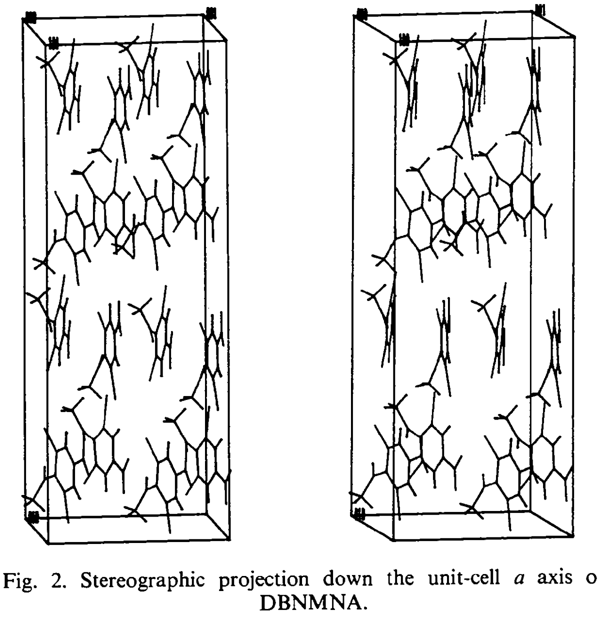

Fig. 2. Stereographic projection down the unit-cell *a* axis of DBNMNA.

(Skapski & Stevenson, 1973) and a polar *c* axis. In *m*NA the least-squares plane through the aromatic ring makes an angle of 59° with the *c* axis. The molecular dipoles of DBNMNA are not, however, as closely aligned as in the monoclinic electro-optic crystal MNA (Lipscomb, Garito & Narang, 1981).

The closest intermolecular contacts in the DBNMNA crystal are shown in Table 2. The shortest interaction (2·5 Å) is between the nitro group oxygen O(2) and the methylamino group hydrogen H(1). This distance is equal to the sum of the van der Waals radii of H and O atoms suggesting that if it exists, hydrogen bonding is weak. However, the amino proton H(1) is located between the two O atoms of the neighboring nitro group in an orientation resembling the 'inside' hydrogen-bonded structure observed for a wide range of substituted nitroanilines. All of the neighboring DBNMNA molecules are ordered in infinite polar chains, closely resembling those in *N*-methyl-4-nitroaniline crystals. This polar ordering may be a structural consequence of these weak NH···O interactions (Panunto, Urbanczyk-Lipkowska, Johnson & Etter, 1987).

DBNMNA shows a powder second harmonic efficiency 80% of that of MNA using a fundamental wavelength of 1·064 μm. Thus the validity of the assignment of the crystal to a polar space group is confirmed. In addition, the electro-optic effects involving coefficients r_{51} and r_{42} are quadratic while those involving r_{13} and r_{33} are linear as is required by *mm*2 point group symmetry (Nahata, Horn & Yardley, 1990).

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Structure of 5-[2-(3-Indolyl)ethyl]-1,3-dimethyluracil 1,3-Dimethyluracil *cis,syn*-Cyclobutane Photodimer

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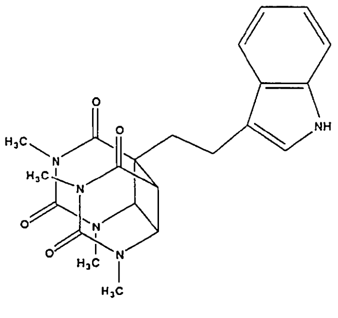
Abstract. 4a-[2-(3-Indolyl)ethyl]-1,3,6,8-tetramethyl-4a,4b,8a,8b-tetrahydrocyclobuta[1,2-*d*:4,3-*d*′]dipyrimidine-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-tetrone, $C_{22}H_{25}N_5O_4$, $M_r = 423{\cdot}52$, triclinic, $P\bar{1}$, $a = 8{\cdot}116$ (4), $b = 15{\cdot}888$ (6), $c = 16{\cdot}226$ (7) Å, $\alpha = 87{\cdot}05$ (3), $\beta = 86{\cdot}28$ (3), $\gamma = 87{\cdot}79$ (3)°, $V = 2083{\cdot}8$ (15) Å^3, $Z = 4$, $D_m = 1{\cdot}34$, $D_x = 1{\cdot}35$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}9$ cm^{-1}, $F(000) = 896$, $T = 298$ K, $R = 0{\cdot}0872$ for 3779 observed data $[F_o > 3\sigma(F_o)]$ of 7155 unique data collected. Hydrogen bonding is observed between the indolyl N—H and the uracil C(4)—O as well as attractive interaction between the uracil C(5)—H and C(4)—O atoms. It is assumed that van der Waals interactions hold layers of hydrogen-bonded molecules that lie parallel to the (011).

Introduction. Cyclobutane-type pyrimidine dimers are the major photoproducts that arise in DNA by UV irradiation. This form of UV damage to DNA is subject to repair by photolyases, enzymes that utilize near-UV and visible light to split dimers back into the original pyrimidine nucleotides (Sancar & Sancar, 1987, 1988). Photolyases bind a cofactor ($FADH_2$) that absorbs light and possibly transfers an electron to the dimer to achieve dimer splitting (Jordan & Jorns, 1988; Heelis & Sancar, 1986).

Many simple photosensitizers split dimers by an electron-transfer process, which produces either the dimer radical cation or the dimer radical anion (Pac & Ishitani, 1988). Tryptophan-containing proteins induce splitting of pyrimidine dimers in DNA (Cochran, Sugasawara & Schultz, 1988; Hélène & Charlier, 1977), probably by electron donation from the indole. Likewise, compounds consisting of a pyrimidine dimer covalently linked to an indole, designed to mimic the intramolecular photosensitization within the photolyase–DNA complex, undergo dimer photosplitting (Kim & Rose, 1988; Young, Kim, Van Camp, Hartman & Rose, 1988; Hartman, Van Camp & Rose, 1987; Van Camp, Young, Hartman & Rose, 1987).

This paper reports the crystal structure of a 1,3-dimethyluracil *cis,syn*-photodimer with a covalently linked indole (1). The crystal structure was found to possess features that help rationalize the exhibited photochemical behavior.



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