MAK, J. C. W. & TROTTER, J. (1965). *Acta Cryst.* **18**, 68–74.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. NSC, 3200A Research Forest Drive, The Woodlands, TX 73381, USA.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
NAHATA, A., HORN, K. A. & YARDLEY, J. T. (1990). *IEEE J. Quantum Electron.* **26**, 1521–1526.
PANUNTO, T. W., URBANCZYK-LIPKOWSKA, A., JOHNSON, R. & ETTER, M. C. (1987). *J. Am. Chem. Soc.* **109**, 7786–7797.
SENEAR, A. E., RAPPORT, M. M., MEAD, J. R., MAYNARD, J. T. & KOEPFLI, J. B. (1946). *J. Org. Chem.* **11**, 378–383.
SINGER, K. D., LALAMA, S. L., SOHN, J. E. & SMALL, R. D. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. I, edited by D. S. CHEMLA & J. ZYSS, pp. 437–468. New York: Academic Press.
SKAPSKI, A. C. & STEVENSON, J. L. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1197–1200.
TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009–1017.
TSUDA, M. (1969). *Bull. Chem. Soc. Jpn*, **42**, 905–908.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.
ZYSS, J. & CHEMLA, D. S. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. I, edited by D. S. CHEMLA & J. ZYSS, pp. 23–191. New York: Academic Press.

Acta Cryst. (1991). C**47**, 1287–1290

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

BY THOMAS L. GROY,* SANG-TAE KIM AND SETH D. ROSE

Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604, *USA*

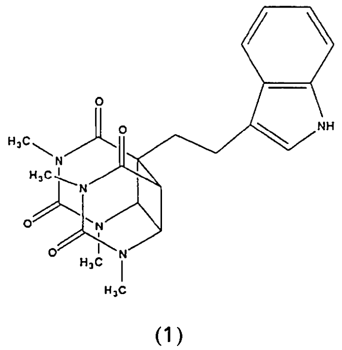
(*Received* 1 *December* 1989; *accepted* 29 *October* 1990)

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, $\alpha = 87{\cdot}05\,(3)$, $\beta = 86{\cdot}28\,(3)$, $\gamma = 87{\cdot}79\,(3)^\circ$, $V = 2083{\cdot}8\,(15)$ 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.



(1)

---

* To whom correspondence should be addressed.

0108-2701/91/061287-04$03.00

Experimental. *Preparation of* 1,3-*dimethyluracil cis,syn-photodimer with a covalently linked indole* (1). The preparation of the compound is reported elsewhere (Kim, Hartman & Rose, 1990). Successive recrystallization of the compound from hot methanol, followed by filtration and drying over a gentle stream of nitrogen in the dark, yielded colorless transparent plates. The selected crystal was cut and mounted on a glass fiber. The crystal, with dimensions 0·15 × 0·10 × 0·17 mm, was dipped into a solution of methanol/ethyl acetate (3:97, by volume) to give a clean outline. Density was measured by flotation in a cadmium chloride–water mixture.

Structure determination. A Siemens *R3m*/*V* diffractometer was used for data collection. Cell parameters were refined by least squares on 25 reflections in the 2θ range 3·5–15·0°. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation in the range $3{\cdot}5 \leq 2\theta \leq 50{\cdot}0°$ using the ω-scan method. The data were corrected for Lorentz and polarization effects. A secondary-extinction correction was applied as defined by Zachariasen (1967). No absorption correction was used. Data with $F_o \geq 3\sigma(F_o)$ were considered observed (3779 of 7155 unique data, $R_{\rm int} = 0{\cdot}0228$). Structure solution was obtained by direct methods (Siemens *SHELXTL-Plus*; Sheldrick, 1988) on a DEC MicroVAX 2000 computer. The indole groups as well as major portions of the uracil dimers were obtained from the solutions with the best combined figure of merit. Difference maps revealed the remaining non-H atoms. The structure was refined in the early stages by full-matrix least squares. In the later stages (after anisotropic thermal parameters were well defined), the refinement was performed by the accelerated full-matrix least-squares technique, in which the inverse matrix is modified after the first cycle without repeating the addition of derivative products and subsequent inversion of the matrix. H atoms were added in idealized positions and refined as atoms riding on their bonding partners. Final conventional $R = 0{\cdot}0872$ and $wR = 0{\cdot}0573$, where $w = 1{\cdot}000/[\sigma^2(F) + 0{\cdot}000102(F^2)]$. The largest peak in the final difference map was 0·34 e Å^{-3} with 0·002 as the final $(\Delta/\sigma)_{\rm max}$. The range of *hkl* was 0 to 9, −18 to 18, and −19 to 19, respectively. Three standard reflections ($\bar{1}0\bar{2}$, $01\bar{2}$ and $1\bar{2}\bar{4}$) were collected every 47 reflections and indicated no degradation (variation of standard intensities < ±1%). The entire structure determination, as well as the production of the plots, was performed by the *SHELXTL-Plus* package. Preliminary indication of the presence of an inversion center was shown using the criteria of Howells, Phillips & Rogers (1950) in the program *CENTEST* written by one of the authors (TLG). *SHELXTL-Plus* also gave similar inversion center indications.

Discussion. The final atomic parameters with their e.s.d.'s are listed in Table 1.* Selected bond lengths and angles, with the associated estimated standard deviations, appear in Table 2. A view of one of the molecules, together with the atom-labeling scheme, is given in Fig. 1. Hydrogen bonding appears to have the major role in stabilizing the crystal structure, as can be seen in Fig. 2. The two C═O bonds involved in hydrogen bonding [C(4*A*)—O(4*A*) and C(4*B*)—O(4*B*)] are slightly longer than those that are not [C(2*A*)—O(2*A*) and C(2*B*)—O(2*B*)]. The hydrogen bonds occur in N(1*iB*)—H(1*iB*)···O(4*A*) and N(1*iB*)—H(1*iB*)···O(4′*A*). The N(1*iB*)···O(4*A*) and N(1*iB*)···O(4′*A*) intermolecular distances are 3·054 and 2·955 Å, respectively, and C(5′*B*)···O(4*A*) is 3·376 Å. This proximity of C(5′*B*) to O(4*A*) gives indications of an attractive interaction involving C(5′*B*)—H(5′*B*)···O(4*A*). It was previously found that the C(5) H atom of a pyrimidine dimer was sufficiently acidic to undergo base-catalyzed exchange with solvent *via* a deprotonated intermediate (Hartman, Van Camp & Rose, 1987). The ease of this exchange was attributed to the delocalization of C(5) lone-pair electrons into the adjacent C(4) carbonyl group of the dimer anion. In (1), polarization of the C(5′)$^{\delta-}$—H$^{\delta+}$ bond might be stabilized by a similar delocalization of charge from C(5′) into the C(4′) carbonyl group, thereby enabling the attractive interaction. There are many other examples of short C—H···O contacts (Sarma & Desiraju, 1987, and references therein).

The indole groups are planar, as previously described for other indoles (Watson, Nagl, Silva, Cespedes & Jakupovic, 1989; Roychowdhury & Basak, 1975; Hanson, 1964), and the uracil dimer has a puckered cyclobutane ring typical of this family of compounds (Flippen-Anderson & Gilardi, 1984; Karle, 1982; Konnert, Gibson, Karle, Khattak & Wang, 1970; Camerman & Camerman, 1970; Adman, Gordon & Jensen, 1968; Gibson & Karle, 1971; Adman & Jensen, 1970). The cyclobutane torsional angles about C(5)—C(6) and C(5′)—C(6′) for molecules *A* and *B* are 16·9 and 15·4°, respectively. These angles can be compared to those of 16·5° in 6-methyluracil *cis,syn*-photodimer (Gibson & Karle, 1971), 17·0° in uracil *cis,syn*-photodimer (Adman & Jensen, 1970) and 17·8° in a dimethyluracil *cis,syn*-photodimer (Flippen-Anderson & Gilardi, 1984). A feature of the intermolecular structure is the existence of layers of hydrogen-bonded molecules parallel to (011) that are held by what are assumed to be van

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53268 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

der Waals interactions. This is illustrated in Fig. 2. A further feature to note is the lack of hydrogen bonding by the O(2) and O(2′) atoms. All the hydrogen bonding occurs with only the O(4) and O(4′) atoms, possibly as a consequence of electron release to O(4) by the adjacent C(5′)—H bond (see above).

If the major conformation of (1) in solution is similar to that in the crystal structure, then electron transfer between dimer and indole portions of the molecule may involve the π systems of the indole and the nearby C(4′) carbonyl group of the dimer. The distance from dimer C(4*A*) to indole C(3*iA*) is only 4·30 Å, and the distance from the former to indole C(5*iA*), an atom that becomes electron rich in excited indoles (Yang, Huang & Yang, 1977), is 6·04 Å. These distances qualitatively account for the high degree of indole fluorescence quenching by the attached dimer in (1), which is a consequence of electron transfer to the dimer within the lifetime of the excited singlet state of the indole (Young, Kim, Van Camp, Hartman & Rose, 1988). Conformational changes that further decrease the distance between electron donor and acceptor might also occur in solution.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}*
N(1*A*)	6735 (6)	850 (3)	− 738 (3)	51 (2)
C(2*A*)	5830 (8)	1136 (4)	− 78 (4)	55 (3)
N(3*A*)	4750 (5)	1839 (3)	− 231 (3)	45 (2)
C(4*A*)	4350 (7)	2171 (3)	− 993 (3)	41 (2)
C(5*A*)	5353 (7)	1842 (3)	− 1743 (3)	38 (2)
C(6*A*)	6858 (7)	1295 (3)	− 1521 (3)	49 (2)
N(1′*A*)	8241 (7)	2505 (4)	− 910 (3)	66 (2)
C(2′*A*)	7607 (10)	3261 (6)	− 689 (4)	73 (3)
N(3′*A*)	6555 (7)	3695 (3)	− 1230 (3)	64 (2)
C(4′*A*)	6101 (8)	3416 (4)	− 1971 (4)	53 (3)
C(5′*A*)	6574 (7)	2525 (3)	− 2123 (3)	46 (2)
C(6′*A*)	7973 (7)	2087 (3)	− 1649 (3)	51 (2)
C(1*eA*)	4150 (7)	1532 (3)	− 2342 (3)	51 (2)
C(2*eA*)	3204 (7)	755 (3)	− 2013 (3)	54 (2)
C(1*iA*)	− 216 (8)	− 1526 (4)	− 2018 (3)	59 (3)
C(2*iA*)	933 (7)	− 917 (3)	− 1944 (3)	50 (2)
C(3*iA*)	792 (7)	− 155 (3)	− 2418 (3)	43 (2)
C(4*iA*)	− 513 (8)	− 46 (3)	− 2952 (3)	49 (2)
C(5*iA*)	− 1680 (7)	− 650 (4)	− 3014 (3)	58 (3)
C(6*iA*)	− 1504 (8)	− 1384 (4)	− 2544 (4)	66 (3)
C(7*iA*)	1025 (8)	1091 (3)	− 3088 (3)	55 (2)
C(8*iA*)	1750 (7)	587 (3)	− 2502 (3)	42 (2)
N(9*iA*)	− 344 (6)	733 (3)	− 3348 (3)	59 (2)
O(2*A*)	5905 (5)	820 (3)	616 (2)	85 (2)
O(2′*A*)	7876 (7)	3574 (3)	− 46 (3)	123 (3)
O(4*A*)	3272 (5)	2724 (2)	− 1057 (2)	59 (2)
O(4′*A*)	5259 (5)	3840 (3)	− 2447 (3)	77 (2)
C(7*A*)	7806 (8)	92 (4)	− 622 (4)	84 (3)
C(7′*A*)	9503 (8)	2113 (4)	− 388 (4)	114 (4)
C(8*A*)	3940 (8)	2217 (4)	499 (3)	77 (3)
C(8′*A*)	5856 (9)	4510 (4)	− 979 (4)	107 (4)
N(1*B*)	− 3673 (6)	4078 (3)	4190 (3)	47 (2)
C(2*B*)	− 4977 (9)	3683 (4)	4558 (3)	56 (3)
N(3*B*)	− 4602 (6)	2957 (3)	5069 (3)	50 (2)
C(4*B*)	− 3075 (7)	2695 (3)	5314 (3)	41 (2)
C(5*B*)	− 1583 (6)	3113 (3)	4883 (3)	36 (2)
C(6*B*)	− 2033 (7)	3709 (3)	4147 (3)	42 (2)
N(1′*B*)	− 2943 (6)	2529 (3)	3286 (3)	55 (2)
C(2′*B*)	− 3366 (9)	1740 (5)	3564 (4)	64 (3)
N(3′*B*)	− 2363 (7)	1305 (3)	4129 (3)	61 (2)
C(4′*B*)	− 939 (9)	1606 (4)	4414 (3)	53 (3)
C(5′*B*)	− 674 (7)	2513 (3)	4235 (3)	41 (2)
C(6′*B*)	− 1558 (7)	2978 (3)	3536 (3)	48 (2)
C(1*eB*)	− 492 (6)	3411 (3)	5535 (3)	45 (2)
C(2*eB*)	− 1330 (6)	4093 (3)	6085 (3)	45 (2)
C(1*iB*)	− 1634 (8)	6175 (3)	8005 (4)	60 (3)
C(2*iB*)	− 1681 (7)	5631 (3)	7371 (3)	49 (2)
C(3*iB*)	− 677 (7)	4897 (3)	7391 (3)	42 (2)
C(4*iB*)	353 (7)	4738 (4)	8052 (3)	48 (2)
C(5*iB*)	413 (8)	5301 (4)	8683 (3)	63 (3)
C(6*iB*)	− 599 (8)	6003 (4)	8655 (4)	66 (3)
C(7*iB*)	704 (7)	3675 (3)	7210 (3)	53 (2)
C(8*iB*)	− 430 (7)	4207 (3)	6854 (3)	41 (2)
N(9*iB*)	1176 (6)	3982 (3)	7934 (3)	59 (2)
O(4*B*)	− 2909 (4)	2138 (2)	5848 (2)	50 (1)
O(4′*B*)	− 53 (6)	1162 (2)	4856 (2)	75 (2)
O(2*B*)	− 6405 (5)	3917 (3)	4493 (2)	81 (2)
O(2′*B*)	− 4590 (6)	1408 (3)	3341 (3)	104 (2)
C(7*B*)	− 3961 (7)	4855 (3)	3686 (3)	73 (3)
C(7′*B*)	− 3814 (8)	2916 (4)	2604 (3)	94 (3)
C(8*B*)	− 6019 (7)	2492 (4)	5427 (4)	89 (3)
C(8′*B*)	− 2891 (9)	466 (4)	4425 (4)	99 (4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

C(2*A*)—O(2*A*)	1·212 (7)	C(4*A*)—O(4*A*)	1·221 (7)
C(5*A*)—C(6*A*)	1·523 (7)	C(5*A*)—C(5′*A*)	1·573 (7)
C(6*A*)—C(6′*A*)	1·577 (8)	C(2′*A*)—O(2′*A*)	1·215 (9)
C(4′*A*)—O(4′*A*)	1·224 (7)	C(5′*A*)—C(6′*A*)	1·536 (8)
C(2*B*)—O(2*B*)	1·213 (8)	C(4*B*)—O(4*B*)	1·217 (6)
C(5*B*)—C(6*B*)	1·539 (7)	C(5*B*)—C(5′*B*)	1·582 (7)
C(6*B*)—C(6′*B*)	1·587 (7)	C(2′*B*)—O(2′*B*)	1·225 (9)
C(4*B*)—O(4′*B*)	1·227 (7)	C(5′*B*)—C(6′*B*)	1·525 (7)
C(6*A*)—C(5*A*)—C(5′*A*)	88·0 (4)	C(5*A*)—C(6*A*)—C(6′*A*)	90·0 (4)
C(5*A*)—C(5′*A*)—C(6′*A*)	89·7 (4)	C(6*A*)—C(6′*A*)—C(5′*A*)	87·4 (4)
C(6*B*)—C(5*B*)—C(5′*B*)	87·7 (3)	C(5*B*)—C(6*B*)—C(6′*B*)	89·8 (4)
C(5*B*)—C(5′*B*)—C(6′*B*)	90·4 (4)	C(6*B*)—C(6′*B*)—C(5′*B*)	88·0 (4)

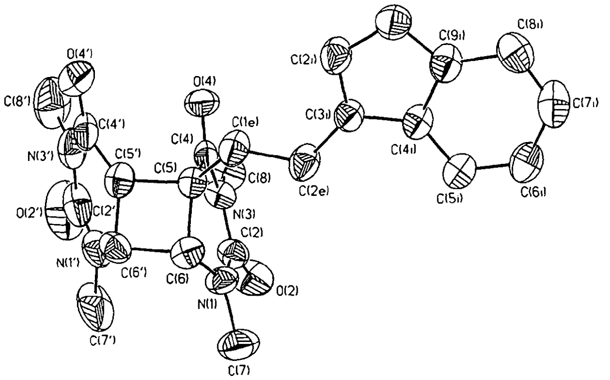


Fig. 1. Perspective view of one of the molecules, with the atom-labeling scheme. H atoms are omitted for clarity. Thermal ellipsoids are depicted at the 50% probability level.

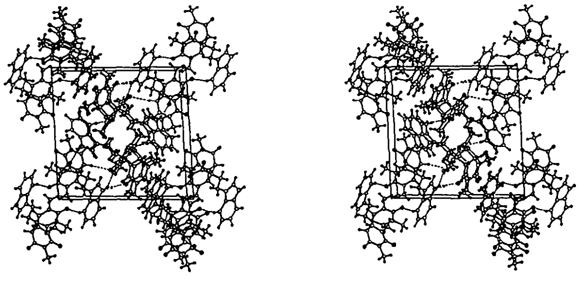


Fig. 2. Stereoview of the hydrogen-bonded layer structure as seen down the *a* axis, with the *b* axis to the right and the *c* axis down. Hydrogen bonds are represented by dashed lines.

References

ADMAN, E., GORDON, M. P. & JENSEN, L. H. (1968). *Chem. Commun.* pp. 1019–1020.
ADMAN, E. & JENSEN, L. H. (1970). *Acta Cryst.* **B26**, 1326–1334.
CAMERMAN, N. & CAMERMAN, A. (1970). *J. Am. Chem. Soc.* **92**, 2523–2527.
COCHRAN, A. G., SUGASAWARA, R. & SCHULTZ, P. G. (1988). *J. Am. Chem. Soc.* **110**, 7888–7890.
FLIPPEN-ANDERSON, J. L. & GILARDI, R. (1984). *Acta Cryst.* **C40**, 1957–1960.
GIBSON, J. W. & KARLE, I. L. (1971). *J. Cryst. Mol. Struct.* **1**, 115–121.
HANSON, A. W. (1964). *Acta Cryst.* **17**, 559–568.
HARTMAN, R. F., VAN CAMP, J. R. & ROSE, S. D. (1987). *J. Org. Chem.* **52**, 2684–2689.
HEELIS, P. F. & SANCAR, A. (1986). *Biochemistry,* **25**, 8163–8166.
HÉLÈNE, C. & CHARLIER, M. (1977). *Photochem. Photobiol.* **25**, 429–434.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.
JORDAN, S. P. & JORNS, M. S. (1988). *Biochemistry,* **27**, 8915–8923.
KARLE, I. L. (1982). *Acta Cryst.* **B38**, 1016–1018.
KIM, S. T., HARTMAN, R. F. & ROSE, S. D. (1990). *Photochem. Photobiol.* **52**, 789–794.
KIM, S. T. & ROSE, S. D. (1988). *Photochem. Photobiol.* **47**, 725–729.
KONNERT, J., GIBSON, J. W., KARLE, I. L., KHATTAK, M. N. & WANG, S. Y. (1970). *Nature (London)*, **227**, 953–954.
PAC, C. & ISHITANI, O. (1988). *Photochem. Photobiol.* **48**, 767–785.
ROYCHOWDHURY, P. & BASAK, B. S. (1975). *Acta Cryst.* **B31**, 1159–1163.
SANCAR, A. & SANCAR, G. B. (1988). *Ann. Rev. Biochem.* **57**, 29–67.
SANCAR, G. B. & SANCAR, A. (1987). *Trends Biochem. Sci.* **12**, 259–261.
SARMA, J. A. R. P. & DESIRAJU, G. R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 1195–1202.
SHELDRICK, G. M. (1988). *SHELXTL-Plus.* Release 3.4 for Siemens *R3m/V* crystallographic system. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
VAN CAMP, J. R., YOUNG, T., HARTMAN, R. F. & ROSE, S. D. (1987). *Photochem. Photobiol.* **45**, 365–370.
WATSON, W. H., NAGL, A., SILVA, M., CESPEDES, C. & JAKUPOVIC, J. (1989). *Acta Cryst.* **C45**, 1322–1324.
YANG, N. C., HUANG, A. & YANG, D.-D. H. (1977). *J. Am. Chem. Soc.* **99**, 8060–8061.
YOUNG, T., KIM, S. T., VAN CAMP, J. R., HARTMAN, R. F. & ROSE, S. D. (1988). *Photochem. Photobiol.* **48**, 635–641.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1991). C47, 1290–1293

2,3-Dihydro-5,7-diphenyl-1,4-diazepinium Perchlorate Hemihydrate

BY DOUGLAS LLOYD

Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

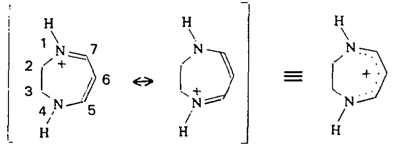
AND GEORGE FERGUSON* AND BARBARA L. RUHL

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

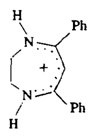
(*Received* 26 *June* 1990; *accepted* 15 *November* 1990)

Abstract. $C_{17}H_{17}N_2^+.ClO_4^-.0{\cdot}5H_2O$, $M_r = 357{\cdot}8$, triclinic, $P\bar{1}$, $a = 9{\cdot}158\,(2)$, $b = 13{\cdot}115\,(2)$, $c = 8{\cdot}372\,(2)$ Å, $\alpha = 95{\cdot}15\,(2)$, $\beta = 107{\cdot}28\,(2)$, $\gamma = 72{\cdot}50\,(2)°$, $V = 915{\cdot}7\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 2{\cdot}3$ cm^{-1}, $F(000) = 374$, $T = 293$ K, $R = 0{\cdot}074$, $wR = 0{\cdot}083$ for 2007 observed data. The crystal structure contains discrete diazepinium cations, perchlorate anions and water molecules linked by a network of hydrogen bonds. The cation contains a five-membered delocalized 1,5-diazapentadienium chain [N—C—C—C—N; mean C—C 1·395 (6), mean C—N 1·332 (6) Å] in a helical conformation. The perchlorate anion and water molecules are disordered.

Introduction. An X-ray structure determination of the 2,3-dihydro-1,4-diazepinium cation (I) (Ferguson, Ruhl, Wieckowski, Lloyd & McNab, 1984) has shown that it consists of a delocalized vinamidinium (3-amino-2-propeniminium) system [N(4),C(5–7),N(1)], whose ends are linked through an ethylene bridge [C(2,3)]. Phenyl substituents attached to a dihydrodiazepinium ring are known to interact electronically with the vinamidinium system (Lloyd, Mackie, McNab, Tucker & Marshall, 1976; Butler, Lloyd, McNab, Marshall & Tucker, 1989); this is evident from both the spectroscopic and chemical properties. It was of interest, therefore, to study structural details of a phenyl derivative, and the 5,7-diphenyl derivative (II) has accordingly been investigated.



(I)



(II)

---

* E-mail address: CHMFERG@VM.UOGUELPH.CA

0108-2701/91/061290-04$03.00