Tableau 2. *Liaisons intermoléculaires courtes*

O(21)–H(O21)···O(3)=C(3)	H(O21)···O(3)	2,32 (2) Å	O(21)–H(O21)···O(3)	158 (5)°
(1) (2)	O(21)···O(3)	3,087 (6)	H(O21)···O(3)=C(3)	117 (5)
C(20)=O(20)···H(1*A*)–C(1)	O(20)···H(1*A*)	2,56 (2)	O(20)···H(1*A*)–C(1)	124 (5)
(1) (2)	O(20)···C(1)	3,226 (6)	C(20)=O(20)···H(1*A*)	150 (5)

Code de symétrie: (1) x,y,z; (2) $\frac{1}{2}-x$, $2-y$, $\frac{1}{2}+z$.

conformes à ce qui pouvait être attendu. Cependant, on peut observer un raccourcissement important de la liaison C(17)–C(20): $1{,}47_1$ Å. Cette distance inhabituelle pour une liaison σ s'explique par une forte conjugaison des liaisons C(16)=C(17) et C(20)=O(20). La conformation de la chaîne latérale est en conséquence inhabituelle; la liaison C(20)–O(20) éclipse la liaison C(17)–C(13) avec un angle de torsion O(20)–C(20)–C(17)–C(13) égal à 8°, alors que dans les corticostéroïdes cet angle est voisin de 95°. Cette orientation particulière a déjà été observée pour la chaîne $COCH_3$-17β de la molécule de époxy-16α,17α pregnènolone (Hazel, Weeks & Osawa, 1976). L'angle de torsion O(20)–C(20)–C(21)–O(21) reste égal à une valeur classique, soit 3°.

Le contact intramoléculaire O(20)···H(O21) est court: 2,23 Å avec O(20)···H(O21)–O(21) égal à 111°.

D'autre part, l'inspection de Fig. 1(*a*), (*b*) et surtout (*c*) montre que les cycles *B*, *C* et *D* de ce stéroïde possèdent chacun un pseudo-élément de symétrie. Le cycle *B* de forme chaise est symétrique autour de C(10)–C(7), le cycle *C* (analogue en conformation au cycle *A*) l'est autour de l'axe [C(9)–C(11)]···[C(13)–C(14)] alors que le cycle *D* l'est autour de l'axe [C(16)–C(17)]–C(14). De plus, il faut remarquer la valeur élevée de l'angle dièdre C(12)–C(13)–C(14)–C(8).

Sur la Fig. 2, sont présentées les vues de la molécule en projection dans le repère *D* (Bally, Lepicard & Surcouf, 1977).

La Fig. 3 montre l'organisation cristalline. Une liaison hydrogène O(21)–H(O21)···O(3) et un contact de van der Waals court C(1)–H(1*A*)···O(20) (Tableau 2) assurent la formation de chaînes infinies centrées sur les axes binaires hélicoïdaux parallèles à l'axe *c*.

L'auteur remercie la Société Roussel-Uclaf et en particulier MM R. Bucourt, L. Nedelec et J. P. Raynaud de lui avoir proposé cette étude et fourni un échantillon du stéroïde étudié.

Références

ALLEN, W. S. & BERNSTEIN, S. (1955). *J. Am. Chem. Soc.* **77**, 1028–1032.

BALLY, R., LEPICARD, G. & SURCOUF, E. (1977). *Acta Cryst.* B**33**, 613–615.

DELETTRÉ, J., MORNON, J. P. & LEPICARD, G. (1979). En préparation.

HAZEL, J. P., WEEKS, C. M. & OSAWA, Y. (1976). *Cryst. Struct. Commun.* **5**, 103–106.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain, Belgique.

SURCOUF, E. (1979). *Acta Cryst.* B35, 2638–2642.

Acta Cryst. (1979). B**35**, 2746–2749

3,4;13,14-Dibenzo-6,6,11,11-tetramethyl-1,8,9-*cis*-tricyclo[7.5.0.$0^{2,8}$]tetradecane-5,12-dione

BY KWO-TSAIR WEI AND DONALD L. WARD

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, *USA*

(*Received* 21 *September* 1977; *accepted* 12 *June* 1979)

Abstract. $C_{26}H_{28}O_2$, orthorhombic, $Pna2_1$, a = 26·648 (8), b = 9·517 (3), c = 7·992 (3) Å, Z = 4, M_r = 372·81, D_x = 1·221 Mg m^{-3}; the material was recrystallized from acetone at room temperature. The lack of symmetry in the dimer molecule is a consequence of the *cis* and *trans* ring junctions at the cyclo-

0567-7408/79/112746-04$01.00

butane ring and is illustrated by the angles of 40·7 and 27·8° between the planes of the two benzene rings, respectively, and the plane of the cyclobutane ring.

Introduction. Studies of the photodimerization of 2,3-benzo-6,6-dimethyl-2,4-cycloheptadienone indicate that it yields two crystalline dimers (Biefeld & Barnett, 1974; Hart, Miyashi, Buchanan & Sanson, 1974; Hart & Suzuki, 1975). Through the identity and stereochemistry of the two products, reaction intermediates have been identified and reaction mechanisms have been proposed. To explore the generality of the photochemistry of the 6,6-dimethyl compound, studies of the photodimerization of 2,3-benzo-7,7-dimethyl-2,4-cycloheptadienone were undertaken (see Fig. 1). Mass and NMR spectra clearly established the presence of the cyclobutane ring and the absence of a symmetry plane or axis in the dimer molecule (Dunkelblum, Hart & Suzuki, 1977); the crystal structure investigation was undertaken to determine the molecular structure.

The diffraction conditions $0kl$: $k + l = 2n$, $h0l$: $h = 2n$, the absence of other unrelated conditions and the orthorhombic symmetry indicate the space groups $Pna2_1$ and $Pnam$. Diffraction data were measured at 298 K with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings of 12 reflections in the range $35° \leq 2\theta \leq 39°$ for which the α_1,α_2 doublet was clearly resolved (λ for Mo $K\alpha_1$ = 0·70926 Å). The 1761 unique reflections [including 371 'unobserved' for which $I < \sigma(I)$] were collected for $2\theta < 50°$ using the θ–2θ scan method: scan speed 1° (2θ) min^{-1}; 10 s backgrounds; scan range 1° (2θ) plus the α_1–α_2 divergence; and three standard reflections measured after every 100 data were used to scale the data (decay ~1%, random fluctuations ±2%). The data were reduced and the standard deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976). The least-squares refinement weights were calculated from the standard deviations of the structure factors by $w = 1/[\sigma^2 + (0{\cdot}02F)^2]$; an absorption correction (μ for Mo $K\alpha$ = 0·04 mm^{-1}) was not applied but an extinction correction was applied to the data by $\text{FOBS}_{\text{cor}} = \text{FOBS}\ (1{\cdot}0 + \text{EF} \times \text{RAWI})$ where RAWI is the raw intensity and EF = $2{\cdot}0 \times 10^{-7}$ (Stout & Jensen, 1968). (EF was determined graphically from FOBS and FCALC of the 10 strongest reflections and was not included as a parameter in the least-squares refinement.)

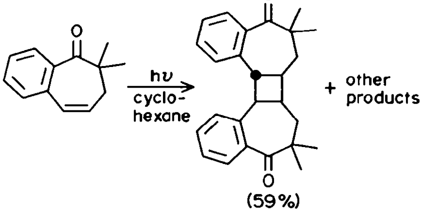

Fig. 1. The photosynthesis of the title compound.

The crystal structure was solved in space group $Pna2_1$ ($Pnam$ was not considered possible due to $Z = 4$ and the spectral evidence of a non-symmetrical molecule) using the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study include *ORTEP* (Johnson, 1965), the entire system of Zalkin's (1974) programs and programs written and/or modified locally.

Due to the limited memory size of the CDC6500 computer used, the 364 atomic parameters and one scale factor were separated into two blocks for full-matrix least-squares refinement; the atomic parameters of the cyclobutane ring C atoms and the scale factor were included in both blocks. The structure was refined to $R_1 = (\sum |F_o - F_c|)/\sum F_o = 0{\cdot}064$, $R_2 = \{[\sum w(F_o - F_c)^2]/\sum w(F_o)^2\}^{1/2} = 0{\cdot}043$; $R_1 = 0{\cdot}109$ including the zero-weighted data [$I \leq \sigma(I)$], and the standard deviation of an observation of unit weight = 0·955; the atomic parameters are listed in Table 1.* The average and maximum shift-to-error ratios for the last cycle of least-squares refinement were 0·057 and 0·281 for non-hydrogen atoms and 0·076 and 0·341 for H atoms. The final difference map showed densities ranging from +0·39 to −0·42 e Å^{-3} with no indication of incorrectly placed or missing atoms. The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H atoms, and the anomalous-scattering factors of Cromer & Liberman (1970) were used for the non-hydrogen atoms. Interatomic distances and angles are shown in Fig. 2.

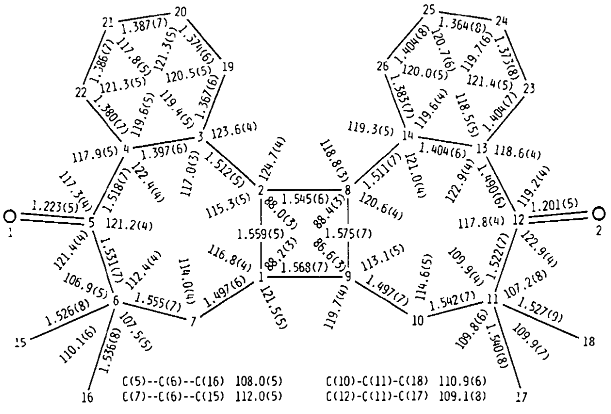

Fig. 2. Bond distances (Å) and angles (°) and their estimated standard deviations.

---

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34537 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and* H-*atom temperature factors*

Fractional coordinates are × 10^4 (× 10^3 for H); temperature factors are in Å^2.

	x	y	z		x	y	z	B_{iso}
O(1)	7240 (1)	273 (4)	2908 (6)	H(1)	885 (2)	175 (6)	167 (9)	7·8 (15)
O(2)	10108 (1)	3432 (4)	6836 (6)	H(2)	835 (1)	90 (3)	483 (4)	0·1 (7)
C(1)	8627 (2)	2102 (5)	2907 (8)	H(3)	823 (2)	380 (5)	183 (7)	4·7 (11)
C(2)	8604 (1)	752*	4009 (6)	H(4)	798 (2)	299 (5)	376 (7)	4·5 (13)
C(3)	8490 (2)	−594 (5)	3077 (6)	H(5)	938 (1)	81 (4)	399 (6)	2·3 (9)
C(4)	8029 (2)	−674 (5)	2254 (6)	H(6)	928 (2)	328 (6)	345 (7)	6·7 (15)
C(5)	7650 (2)	519 (5)	2289 (6)	H(7)	858 (1)	308 (4)	628 (6)	2·8 (10)
C(6)	7768 (2)	1943 (5)	1489 (7)	H(8)	863 (1)	433 (4)	517 (5)	0·9 (7)
C(7)	8140 (2)	2827 (6)	2557 (9)	H(9)	774 (2)	118 (5)	−90 (6)	3·2 (12)
C(8)	9124 (2)	1155 (5)	4714 (6)	H(10)	838 (3)	109 (8)	−32 (10)	11·0 (21)
C(9)	9017 (2)	2720 (5)	4182 (7)	H(11)	810 (3)	243 (9)	−87 (12)	9·7 (24)
C(10)	8837 (2)	3616 (6)	5601 (8)	H(12)	710 (2)	305 (5)	238 (7)	4·3 (13)
C(11)	9258 (2)	4245 (5)	6690 (7)	H(13)	703 (2)	230 (5)	71 (7)	4·0 (13)
C(12)	9670 (2)	3158 (5)	6955 (6)	H(14)	737 (2)	359 (6)	79 (7)	3·9 (14)
C(13)	9517 (2)	1730 (4)	7524 (6)	H(15)	965 (3)	522 (8)	477 (12)	10·4 (27)
C(14)	9245 (2)	796 (5)	6511 (7)	H(16)	977 (2)	586 (6)	655 (9)	6·5 (15)
C(15)	7974 (3)	1644 (9)	−258 (9)	H(17)	922 (2)	620 (6)	591 (6)	4·3 (13)
C(16)	7276 (3)	2777 (9)	1364 (12)	H(18)	933 (2)	504 (5)	911 (6)	3·5 (12)
C(17)	9484 (3)	5542 (7)	5817 (12)	H(19)	891 (3)	380 (10)	897 (11)	12·4 (29)
C(18)	9060 (3)	4651 (9)	8415 (11)	H(20)	882 (2)	519 (5)	814 (7)	3·9 (14)
C(19)	8808 (2)	−1720 (5)	3031 (6)	H(21)	914 (2)	−169 (4)	357 (5)	3·2 (11)
C(20)	8676 (2)	−2923 (5)	2186 (7)	H(22)	888 (1)	−362 (4)	208 (5)	0·9 (8)
C(21)	8219 (2)	−3035 (6)	1368 (7)	H(23)	810 (2)	−376 (6)	71 (7)	5·0 (14)
C(22)	7894 (2)	−1901 (6)	1453 (8)	H(24)	756 (2)	−203 (5)	92 (6)	4·4 (12)
C(23)	9664 (2)	1282 (6)	9124 (8)	H(25)	985 (2)	182 (5)	986 (6)	3·7 (12)
C(24)	9524 (2)	−7 (7)	9739 (8)	H(26)	962 (1)	−23 (4)	1088 (6)	1·6 (8)
C(25)	9243 (2)	−887 (7)	8770 (8)	H(27)	911 (2)	−182 (5)	913 (6)	3·5 (11)
C(26)	9100 (2)	−494 (6)	7145 (7)	H(28)	888 (2)	−122 (5)	636 (7)	5·3 (12)

* Parameter held constant during refinement.

Discussion. The molecular structure (see Fig. 3) is consistent with the mass and NMR spectra and shows that the dimer molecule contains *cis* and *trans* ring junctions at the cyclobutane ring, that the unique H atom of the cyclobutane ring is bonded to C(2), and that the two halves of the dimer molecule are oriented in a 'head to head' fashion. The lack of symmetry in the molecule (in particular, the differences in the folding of the two seven-membered rings) can be attributed to the ring-junction differences. The cyclobutane ring is distorted with an average ring bond angle of 87·8 (7)°, average C—C distance of 1·562 (11) Å, average torsion angle of ±22·1 (2)°, and an average C atom displacement of ±0·152 (2) Å from the least-squares plane. The average bond distances for the dimer molecule as a whole are 1·531 (24), 1·385 (14), and 1·212 (11) Å for C—C, C=C and C=O respectively. (The e.s.d.'s listed above in parentheses are the root-mean-square deviations of the quantities from their average values.)

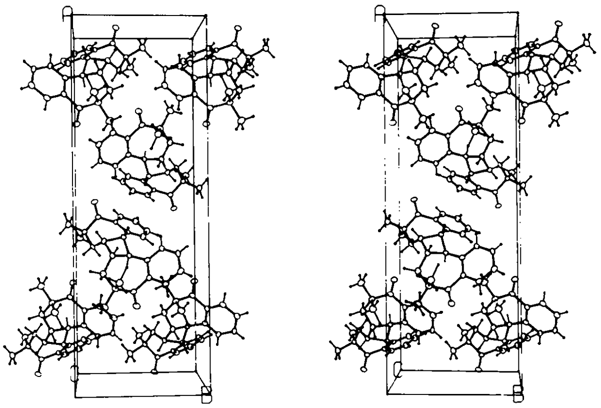

Fig. 3. Packing diagram viewed normal to the *ab* plane (*ORTEP*, Johnson, 1965). Thermal ellipsoids are drawn at the 20% probability level and B_{iso} is set to 0·5 Å^2 for H atoms. The axes are oriented: +**a** ↑ and +**b** →.

Two portions of the dimer molecule, each consisting of a benzene ring, a carbonyl group and adjacent C atoms [C atoms 2, 3, 4, 5, 6, 19, 20, 21, 22 and O(1); C atoms 8, 11, 12, 13, 14, 23, 24, 25, 26 and O(2)] are very similar with respect to torsion angles; no corresponding pair of angles differ by more than 6° and both carbonyl O atoms lie approximately 60–65° in the same direction from the plane of the adjacent benzene ring. Torsion angles involving C(1) and C(7) differ greatly from those involving C(9) and C(10); this is due to the different folding of the two seven-membered rings which place C(7) and O(1) on the same side of the plane of one ring and C(10) and O(2) on opposite sides of the plane of the other ring.

The determination of the structure of this dimer molecule provided additional evidence (Dunkelblum, Hart & Suzuki, 1977) for reaction mechanisms which involve intermediates containing a *trans* C=C bond.

References

BIEFELD, C. G. & BARNETT, B. L. (1974). *Acta Cryst.* B**30**, 2411–2421.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

DUNKELBLUM, E., HART, H. & SUZUKI, M. (1977). *J. Am. Chem. Soc.* **99**, 5074–5082.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HART, H., MIYASHI, T., BUCHANAN, D. N. & SANSON, S. (1974). *J. Am. Chem. Soc.* **96**, 4857–4866.

HART, H. & SUZUKI, M. (1975). *Tetrahedron Lett.* **40**, 3447–3450.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 411–412, equation 17.16. New York: Macmillan.

WEI, K.-T. & WARD, D. L. (1976). *Acta Cryst.* B**32**, 2768–2773.

ZALKIN, A. (1974). Private communication.

Acta Cryst. (1979). B**35**, 2749–2751

The Cyclohexylammonium Salt of Ethyl Hydrogen Phosphate

BY K. ANN KERR*

Departments of Chemistry and Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

J. KEITH FAWCETT

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A8

AND J. C. COPPOLA, DAVID G. WATSON AND OLGA KENNARD†

University Chemical Laboratory, Lensfield Road, Cambridge, England

(*Received* 6 *March* 1979; *accepted* 2 *July* 1979)

Abstract. $C_6H_{14}N^+.C_2H_6O_4P^-$, monoclinic, $A2/a$, $Z = 8$, $a = 18{\cdot}289$ (6), $b = 6{\cdot}026$ (3), $c = 23{\cdot}181$ (8) Å, $\beta = 96{\cdot}86$ (4)°, $V = 2536{\cdot}47$ Å^3, $\rho_{\text{calc}} = 1{\cdot}17$ Mg m^{-3}, μ(Cu $K\alpha$) = $0{\cdot}893$ mm^{-1}. The length of the P–O(ester) bond is 1·579 (5) Å, the P–O(H) bond is 1·559 (4) Å. The hydrogen bond involving the O–H group is relatively short with an O···O distance of 2·542 (6) Å.

Introduction. Kirby & Varvoglis (1967) have shown that there is a linear free-energy relationship between the rate constant for hydrolysis and the pK_a of the leaving group for both mono- and dianions of phosphate esters, ROPO(OH)$_2$. This study is part of a series of structure determinations of monoanions of such esters to determine whether the length of the P–O(ester) bond is correlated with the hydrolysis rate.

Data were collected on a Picker diffractometer with filtered Cu $K\alpha$ radiation, operating in the ω–2θ scan mode with a scan width of $\Delta 2\theta = (2{\cdot}0 + 0{\cdot}285 \tan\theta)°$ and a scan rate of 1° min^{-1}. Background was measured for 40 s at either end of the scan. 2261 independent reflexions were measured below $2\theta = 115°$. Of these, 1525 had intensity significantly above background.

The structure was solved by standard heavy-atom methods after the P atom had been located in a Patterson synthesis. Refinement by full-matrix least squares resulted in a final R value of 0·0803; $R_w = 0{\cdot}0959$. The weighting function used in the final stages of refinement was $w = 1{\cdot}00/[\sigma^2(F) + 0{\cdot}006F^2]$. All H atoms save those on the terminal methyl group were located in a difference synthesis. These have been included in the refinement subject to the constraint that they remain 1·08 Å from the C or N to which they are attached. The H attached to O has not been refined. The terminal methyl group and the quaternary ammonium group were refined as rigid groups.

The refinement was carried out using the *SHELX* (Sheldrick, 1976) system of programs. Scattering factors and anomalous-dispersion terms were taken

---

* To whom correspondence should be addressed.

† External staff, Medical Research Council.

0567-7408/79/112749-03$01.00