Table 8. *Estimated values for the standard deviations in bond lengths* ($\sigma_1$) *and valence angles* ($\sigma_2$), *and indices R*

| | $P_4S_5$ | $P_4S_7$ | $P_4S_{10}$ |
|---|---|---|---|
| $\sigma_1$(Å) | 0·011 | 0·007 | 0·015 |
| $\sigma_2$(°) | 0·45 | 0·3 | 0·7 |
| $R$ | 0·073 | 0·078 | 0·087 |

We wish to thank Professor E. H. Wiebenga for his interest throughout the course of this investigation. The anisotropic least-squares analyses were kindly carried out by Dr J. S. Rollett; the further calculations were done at the Groningen University computing centre. One of us (R.O.) acknowledges support from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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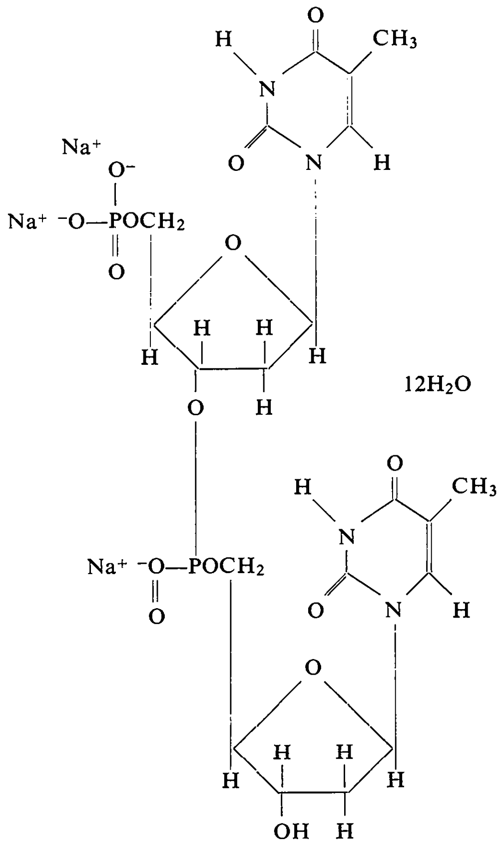
# Crystal data for sodium thymidylyl-(5′ → 3′)-thymidylate-(5′).

By NORMAN CAMERMAN and JAMES TROTTER, *Department of Chemistry, University of British Columbia, Vancouver* 8, *B.C., Canada*

(*Received* 3 *May* 1965)



(I)

Crystals of the dinucleotide, sodium thymidylyl-(5′ → 3′)-thymidylate-(5′) (see I), prepared by the method of Gilham & Khorana (1958) and crystallized from 50% ethanol-water, are colorless plates elongated along *a* with (001) developed. The density was measured by flotation in $CHCl_3$–$CHBr_3$, and the unit-cell dimensions and space group were determined from various rotation, Weissenberg and precession photographs, and on the General Electric Spectrogoniometer.

*Crystal data* (λ, Cu $K\alpha = 1{\cdot}5418$ Å; λ, Mo $K\alpha = 0{\cdot}7107$ Å).

Sodium thymidylyl-(5′ → 3′)-thymidylate-(5′),
$C_{20}H_{25}N_4O_{15}P_2Na_3$, M.W. 692·4
(with $12H_2O$, M.W. 908·6).
Orthorhombic, $a = 16{\cdot}06 \pm 0{\cdot}04$, $b = 15{\cdot}13 \pm 0{\cdot}04$, $c = 15{\cdot}65 \pm 0{\cdot}04$ Å.
$U = 3803$ Å³.
$D_m = 1{\cdot}588$ g.cm⁻³, $Z = 4$, $D_x = 1{\cdot}209$ g.cm$^{-3}$. With $12H_2O$ of hydration per molecule of dinucleotide $D_x = 1{\cdot}587$ g.cm$^{-3}$.
Absorption coefficient for Cu $K\alpha$ X-rays, $\mu = 23$ cm$^{-1}$.
$F(000) = 1904$.
Absent spectra: $h00$ when $h$ is odd, $0k0$ when $k$ is odd. Space group is $P2_12_12$ ($D_2^3$).

Gilham & Khorana (1958) reported $13H_2O$ of hydration on the basis of chemical analysis, but our measured density (1·588 g.cm$^{-3}$) corresponds closely to $12H_2O$ per molecule of dinucleotide ($D_x = 1{\cdot}555$, 1·587, 1·618 g.cm$^{-3}$ for 11, 12, and $13H_2O$ respectively).

The intensities of all reflexions out to $d = 1{\cdot}2$ Å were measured with a scintillation counter and Cu $K\alpha$ radiation, by our usual techniques (see, *e.g.*, Camerman & Trotter, 1965). 953 reflexions (70 % of the total) had intensities above background. A three-dimensional sharpened Patterson function was computed; this was a beautifully detailed distribution, but many efforts to derive the structure by vector superposition methods have been unsuccessful.

Several attempts were made to prepare caesium, rubidium, silver, and thallium salts, but in no case could a crystalline sample be obtained.

The authors are indebted to Dr G. M. Tener for suggesting the problem, for assistance with the preparation of crystal samples, and for many helpful discussions; to Dr M. Sundaralingam and Dr D. G. Watson for helpful discussion; to the U.B.C. Computing Centre for assistance; and to the National Research Council of Canada for financial support, and for the award of a research studentship (to N.C.).

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## The crystal structure of 1,1'-dibenzoylruthenocene.

By James Trotter and Simon H. Whitlow, *Department of Chemistry, University of British Columbia, Vancouver* 8, *B.C., Canada*

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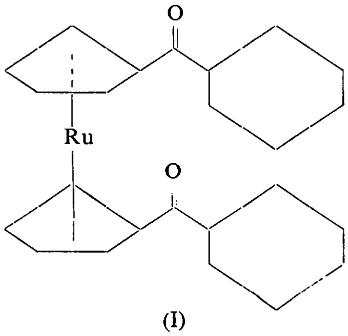
Crystals of 1,1'-dibenzoylruthenocene (I) are golden-yellow leaflets, m.p. 125–126 °C. The unit-cell parameters were determined from rotation, Weissenberg and precession films.



(I)

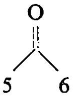
*Crystal data* ($\lambda$, Cu $K\alpha = 1{\cdot}5418$ Å; $\lambda$, Mo $K\alpha = 0{\cdot}7107$ Å).

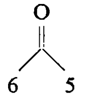
Dibenzoylruthenocene, $C_{24}H_{18}O_2Ru$, M.W. 439·5.
Monoclinic, $a = 7{\cdot}34 \pm 0{\cdot}02$, $b = 12{\cdot}02 \pm 0{\cdot}02$, $c = 20{\cdot}02 \pm 0{\cdot}04$ Å, $\beta = 90°$.
$U = 1766$ Å$^3$.
$D_m$ (flotation in $CCl_4$–$CHBr_3$) $= 1{\cdot}65$, $Z = 4$, $D_x = 1{\cdot}65$ g.cm$^{-3}$.

The diffraction pattern exhibits an interesting series of regions of diffuse scattering, the diffuseness being present only in the $Hkl$ layers of the reciprocal lattice with $H = 2n+1$. In addition the layers with $h = 2n$ show orthorhombic symmetry, but for those with $h = 2n+1$ the symmetry is only monoclinic. This pattern is typical of an order-disorder structure (Dornberger-Schiff, 1956, Sedlacek & Dornberger-Schiff, 1965) built up from rows of molecules parallel to **a**. Within each row the molecular arrangement is perfectly ordered, but the sequence of rows is such that there is no true periodicity in the **b** and **c** directions. The disorder in the stacking must result from the fact that there are at least two energetically equivalent ways in which neighbouring rows can be placed with respect to one another. Since reflexions with $h = 2n$ show no diffuseness, ordered building blocks in the crystal are probably related to neighbouring blocks simply by translation $a/2$.

It seems virtually impossible to deduce the detailed structure since this would involve accounting quantitatively for the diffuse scattering. In fact it is difficult to derive the space group unambiguously; the only definite systematic absence seems to be $0kl$ when $k$ is odd, but in addition $h0l$ are absent for $h = 2n$ when $l = 2n+1$, $0kl$ are weak when $(k/2+l)$ is odd, $2kl$ are weak when $k$ is even. Patterson projections were computed, but no outstanding Ru–Ru peaks were observed, a further indication of disordered ruthenium positions.

Although detailed analysis cannot be carried out, it is possible to indicate the type of molecular arrangement which probably exists in the crystal. Several crystal structures are known in which molecules with five-, six-, and even seven-membered rings show disorder in packing, suggesting that the spatial requirements of these rings are not very different, for example bisindenyl iron (Trotter, 1958) and azulene (Robertson, Shearer, Sim & Watson, 1962). By analogy with these structures it seems likely that in the dibenzoylruthenocene crystal two energetically equivalent molecular packings are possible. The most plausible structure is one with molecules all in a completely eclipsed orientation (I), the two molecular arrangements being related by 180° rotation about an axis parallel to, and midway between the C=O bonds. They may be represented schematically:





Any one row in the **a** direction contains molecules in only one of these orientations, but neighbouring rows are not related.

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