Acta Cryst. (1981). B**37**, 1460–1462

Structure of 3-Cyano-5-oxo-4,4-diphenyl-2-[(triphenoxyphosphonio)oxy]-2-pyrrolinide

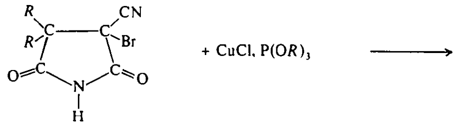
BY L. TOUPET, Y. DÉLUGEARD, J. C. MESSAGER AND M. M. GRANGER

Groupe de Physique Cristalline, ERA au CNRS nº 015, *Université de Rennes, Campus de Beaulieu,*
35042 *Rennes CEDEX, France*

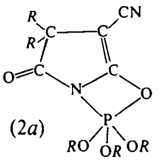
(*Received* 12 *February* 1980; *accepted* 13 *February* 1981)

Abstract. $C_{35}H_{25}N_2O_5P$, triclinic, $P\bar{1}$, $a = 9{\cdot}260\,(4)$, $b = 9{\cdot}870\,(13)$, $c = 16{\cdot}610\,(17)$ Å, $\alpha = 96{\cdot}77\,(20)$, $\beta = 81{\cdot}57\,(32)$, $\gamma = 88{\cdot}16\,(13)^\circ$, $Z = 2$, $D_c = 1{\cdot}30$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·144 mm^{-1}. Three-dimensional intensity data were collected on an Enraf–Nonius automatic three-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and an ω scan mode (scan range = 1·20°). This structure has been refined to an R value of 0·077 for 2269 independent reflexions. The molecule is found to have betainic character.

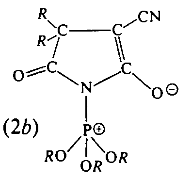
Introduction. The reaction between the CuCl–$P(OPh)_3$ complex and the pyrrolidinedione (1) results in one of the three compounds (2*a*), (2*b*) or (2*c*).



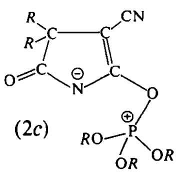
(1)



(2*a*)



(2*b*)



(2*c*)

$R = C_6H_5$

The structure was thought to be that of (2*a*) but it was not unambiguously confirmed by classical methods of spectroscopy (^{13}C NMR, ^{31}P NMR, IR). Furthermore, a comparative study of similar compounds (Ketari & Foucaud, 1978) did not distinguish between (2*a*), (2*b*) and (2*c*) therefore an X-ray analysis was necessary.

Crystals of the title compound were grown by slow evaporation from a solution of anhydrous methanol. The parameters and the space group were determined from Weissenberg photographs. Cell constants were refined by a least-squares analysis of the settings of 66 reflexions. 2269 reflexions with $I > 2\sigma(I)$ were included in the calculations. Neutral-atom scattering factors were obtained from *International Tables for X-ray Crystallography* (1974).

Table 1. *Final positional coordinates* (×10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$ (Willis & Pryor, 1975).

	x	y	z	B_{eq} (Å^2)
P	0·9728 (2)	0·2752 (2)	0·6409 (1)	3·73 (6)
O(1)	1·0215 (6)	0·4256 (5)	0·6515 (3)	6·02 (8)
O(2)	0·8574 (6)	0·5851 (5)	0·9185 (3)	5·63 (7)
O(3)	0·8088 (5)	0·2487 (4)	0·6759 (3)	4·31 (6)
O(4)	0·9855 (5)	0·2200 (4)	0·5465 (3)	4·09 (6)
O(5)	1·0585 (6)	0·1639 (5)	0·6751 (3)	5·82 (7)
N(1)	0·9223 (5)	0·4844 (4)	0·7905 (3)	1·71 (5)
N(2)	1·2120 (8)	0·7700 (7)	0·6242 (4)	5·84 (7)
C(1)	1·0092 (7)	0·5168 (6)	0·7190 (4)	3·44 (6)
C(2)	1·0623 (8)	0·6419 (7)	0·7314 (4)	3·61 (6)
C(3)	1·0259 (8)	0·7017 (6)	0·8213 (4)	3·63 (6)
C(4)	0·9258 (8)	0·5878 (7)	0·8519 (5)	4·01 (6)
C(5)	1·1464 (8)	0·7100 (7)	0·6703 (4)	3·83 (6)
C(6)	0·9325 (8)	0·8363 (7)	0·8390 (4)	3·66 (6)
C(7)	0·9059 (9)	0·9045 (8)	0·9189 (4)	5·26 (6)
C(8)	0·8128 (10)	1·0203 (9)	0·9359 (5)	6·17 (7)
C(9)	0·7463 (10)	1·0698 (8)	0·8771 (6)	6·71 (8)
C(10)	0·7728 (9)	1·0031 (8)	0·7981 (5)	5·01 (7)
C(11)	0·8663 (8)	0·8860 (7)	0·7786 (4)	4·19 (6)
C(12)	1·1676 (8)	0·7083 (6)	0·8605 (4)	3·40 (6)
C(13)	1·1998 (9)	0·6169 (8)	0·9141 (5)	5·17 (6)
C(14)	1·3369 (11)	0·6205 (9)	0·9431 (5)	6·31 (8)
C(15)	1·4413 (9)	0·7110 (11)	0·9183 (6)	6·23 (8)
C(16)	1·4084 (9)	0·8022 (9)	0·8670 (5)	5·32 (7)
C(17)	1·2706 (9)	0·8036 (7)	0·8386 (4)	4·38 (6)
C(18)	0·6828 (7)	0·3207 (6)	0·6594 (5)	3·75 (6)
C(19)	0·5977 (10)	0·3975 (8)	0·7250 (5)	4·75 (6)
C(20)	0·4673 (12)	0·4593 (9)	0·7113 (7)	6·67 (8)
C(21)	0·4254 (10)	0·4426 (9)	0·6342 (8)	6·94 (8)
C(22)	0·5158 (10)	0·3664 (8)	0·5678 (5)	5·30 (7)
C(23)	0·6477 (9)	0·3039 (7)	0·5801 (5)	4·26 (7)
C(24)	1·1221 (8)	0·2102 (7)	0·4932 (4)	3·80 (6)
C(25)	1·2058 (9)	0·0921 (8)	0·4856 (5)	4·86 (7)
C(26)	1·3371 (11)	0·0818 (9)	0·4308 (6)	6·42 (8)
C(27)	1·3772 (10)	0·1883 (11)	0·3846 (5)	6·33 (8)
C(28)	1·2863 (11)	0·3037 (9)	0·3946 (5)	5·39 (7)
C(29)	1·1576 (10)	0·3160 (7)	0·4498 (5)	4·81 (6)
C(30)	1·1494 (9)	0·1769 (7)	0·7382 (5)	4·29 (6)
C(31)	1·2931 (11)	0·1293 (9)	0·7146 (6)	6·28 (8)
C(32)	1·3814 (11)	0·1353 (13)	0·7753 (10)	9·19 (9)
C(33)	1·3291 (17)	0·1847 (11)	0·8450 (9)	5·61 (7)
C(34)	1·1846 (17)	0·2272 (10)	0·8756 (6)	7·87 (9)
C(35)	1·0887 (10)	0·2236 (8)	0·8175 (5)	5·68 (7)

0567-7408/81/071460-03$01.00

Table 2. *Atomic coordinates for* H *atoms*

	x	*y*	*z*
H(C7)	0·9590	0·8662	0·9650
H(C8)	0·7922	1·0695	0·9955
H(C9)	0·6758	1·1581	0·8907
H(C10)	0·7212	1·0413	0·7524
H(C11)	0·8866	0·9356	0·7187
H(C13)	1·1210	0·5455	0·9318
H(C14)	1·3630	0·5504	0·9833
H(C15)	1·5446	0·7130	0·9396
H(C16)	1·4876	0·8729	0·8488
H(C17)	1·2448	0·8737	0·7992
H(C19)	0·6275	0·4088	0·7856
H(C20)	0·3974	0·5176	0·7606
H(C21)	0·3263	0·4892	0·6253
H(C22)	0·4848	0·3560	0·5084
H(C23)	0·7169	0·2459	0·5304
H(C25)	1·1750	0·0119	0·5205
H(C26)	1·4055	−0·0072	0·4247
H(C27)	1·4739	0·1797	0·3428
H(C28)	1·3167	0·3837	0·3593
H(C29)	1·0894	0·4046	0·4563
H(C31)	1·3339	0·0922	0·6528
H(C32)	1·4944	0·0991	0·7569
H(C33)	1·3998	0·1861	0·8953
H(C34)	1·1455	0·2644	0·9370
H(C35)	0·9756	0·2579	0·8347

The structure was solved with the program *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map computed with the set of best consistency (COMBFOM = 2·6136) revealed 41 of the 43 heavy atoms. The two remaining heavy atoms were located after a Fourier synthesis.

Refinement [program *ORFLS* (Busing, Martin & Levy, 1962)] of the atomic positions with isotropic temperature factors gave $R = 0{\cdot}13$. This residual R decreased to 0·10 with anisotropic temperature factors. Then a Fourier synthesis revealed all the H atoms of the five aromatic rings. These atoms were introduced in the structure-factor calculations with arbitrary temperature factors, but were not refined. The values of the final residuals $R = \sum\left||F_o| - |F_c|\right|/\sum|F_o|$ and $R_w = \left|\sum\left||F_o| - |F_c|\right|^2/\sum|F_o|^2\right|^{1/2}$ were 0·079 and 0·077 respectively.

The final atomic coordinates are given in Table 1 for the heavy atoms and in Table 2 for the H atoms, their standard deviations being in a reasonable range.*

Discussion. The bond distances and angles, with their standard deviations, are shown in Fig. 1. The e.s.d.'s vary from 0·005 to 0·022 Å for the bond lengths. An *ORTEP* drawing (Johnson, 1965) of the molecule is given in Fig. 2. The structure of the studied compound is then the phosphonium betaine (2*c*). There is no ambiguity in this result: the phosphonium part $[P^+(OC_6H_5)_3]$ of the molecule has a regular tetrahedral geometry and the negative charge, arbitrarily located on the nitrogen atom N(1), is delocalized along the O(2)–C(4)–N(1)–C(1)–C(2)–C(5)–N(2) chain. The bond distances and the planarity (Table 3) of the

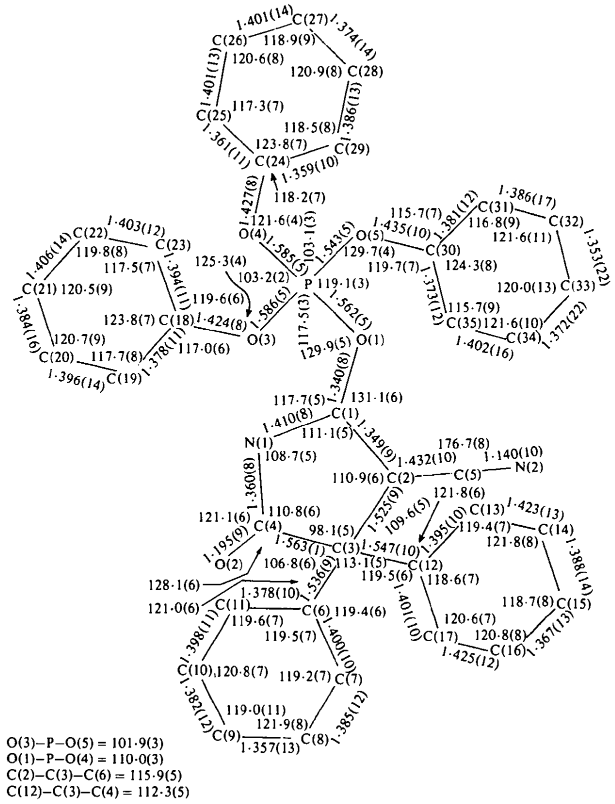


Fig. 1. The numbering system, bond lengths (Å) and valence angles (°) with standard deviations in parentheses.

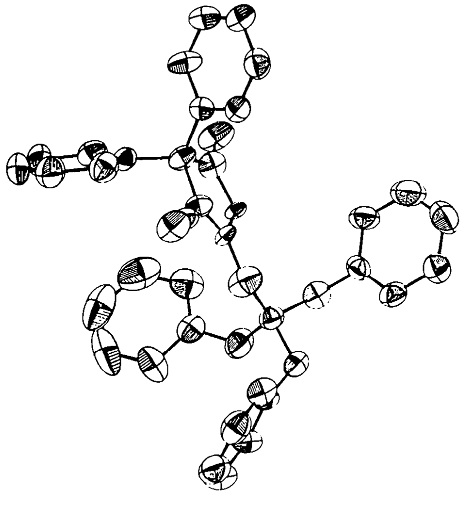


Fig. 2. Perspective view of the molecule with thermal ellipsoids at 50% probability.

---

* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35932 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances* (Å) *of atoms from the least-squares plane of the five-membered ring with e.s.d.'s in parentheses*

$$-0{\cdot}8554X + 0{\cdot}4592Y - 0{\cdot}2397Z + 10{\cdot}4735 = 0.$$

C(1)	−0·029 (16)	C(4)	0·019 (14)
C(2)	0·039 (18)	N(1)	0·004 (12)
C(3)	−0·032 (16)		

five-membered ring confirm this delocalization which furthermore may explain the stability of such a compound. Indeed, isomerization of 2(*b*) is impossible (Ketari & Foucaud, 1978).

The interatomic distances and bond angles of the phenyl rings do not differ significantly from the expected values. Their mean values are 1·387 Å and 120° respectively. Indeed these five rings are coplanar within 0·018 Å. The closest intermolecular non-H atom contact of the structure is 3·33 Å. The shortest intermolecular O···H or N···H distance is 2·54 Å and is too long to be considered a hydrogen-bonding interaction. The packing of the molecules is thus determined by van der Waals forces.

We thank Dr Ketari and Professor A. Foucaud who suggested this work.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

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

Ketari, R. & Foucaud, A. (1978). *Tetrahedron Lett.* **46**, 4515–4518.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1981). B**37**, 1462–1465

Structure of *trans*-3-(Diphenylmethylene)-4-morpholinocarbonyl-5-(*p*-nitrophenyl)tetrahydro-2-furanone

By John Aupers and Peter F. Lindley

Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

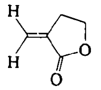
and Ahmet E. Baydar and Gerhard V. Boyd

Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX, England

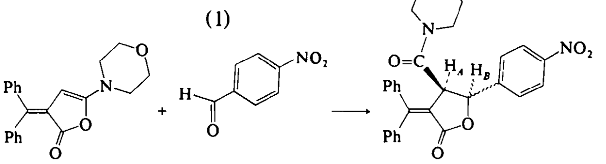
(*Received* 8 *January* 1981; *accepted* 17 *February* 1981)

Abstract. $C_{28}H_{24}N_2O_6$, orthorhombic, *Pbca*, a = 11·093 (2), b = 16·728 (4), c = 25·537 (6) Å, Z = 8, D_c = 1·36 Mg m^{-3}, μ(Cu $K\alpha$) = 0·805 mm^{-1}. The structure was solved by multisolution direct methods and refined by a full-matrix least-squares method to R = 0·049 for 2989 reflections. The compound formed by the 'acyl-ene' reaction between morpholinobutenolide and *p*-nitrobenzaldehyde has a *trans* configuration of protons across the C(4)–C(5) bond.

Introduction. The discovery that various naturally occurring sesquiterpene α-methylene-γ-lactones (1) possess tumour-inhibiting properties has stimulated the search for simpler lactones with physiological activity [for leading references see Kupchan, Hemingway, Werner & Karim (1969) and Lee, Ibuka, Kim, Vestal & Hall (1975)]. General syntheses of α-methylene-γ-lactones continue to be developed, one of which is the 'acyl-ene' reaction (Boyd, Monteil, Lindley & Mahmoud, 1978). An example of this is the formation of a mixture of the substituted *cis*- and *trans*-lactones (3) when the morpholinobutenolide (2) is treated with *p*-nitrobenzaldehyde (Baydar & Boyd, 1978). The isomers were separated by fractional crystallization



(1)



(2) (3)