CRIADO, A. & MUÑOZ, A. (1993). *Acta Cryst.* B49, 726–729
DUNITZ, J. D., SCHOMAKER, V. & TRUEBLOOD, K. N. (1988). *J. Phys. Chem.* 92, 856–867.
ECOLIVET, C., BERTAULT, M., MIERZEJEWSKI, A. & COLLET, A. (1987). *Dynamics of Molecular Crystals*, edited by J. LACOMTE. Amsterdam: Elsevier Science Publishers.
ETRILLARD, J., SOUGOTI, M., TOUDIC, B. & BOURGES, P. (1994). Private communication.
ETXEBARRIA, I., PÉREZ-MATO, J. M. & MADARIAGA, G. (1992). *Phys. Rev. B*, 46, 2264–2274.
FILIPPINI, G. & GAVEZZOTTI, A. (1993). *Acta Cryst.* B49, 868–880.
FILIPPINI, G. & GRAMACCIOLI, C. M. (1989). *Acta Cryst.* A45, 261–263.
FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B (1976). *Acta Cryst.* A32, 259–264.
GRANGER, M. M. & COILLOT, M. F. (1985). *Acta Cryst.* C41, 542–543.
ISHII, K., NAKAYAMA, H., SAKATO, T. & KANO, H. (1992). *J. Phys. Soc. Jpn*, 61, 2317–2326.
KIRIN, D. & PAWLEY, G. S. (1982). *Chem. Phys Lett.* 85(3), 298–301.
MUÑOZ, A. & CRIADO, A. (1992). *Acta Cryst.* B48, 302–306.
PERETTI, P. & RANSON, T. (1979). *J. Raman Spectrosc.* 8, 209–212.

PERTSIN, A. J. & KITAIGORODSKY, A. I. (1987). *The Atom–Atom Potential Method*, Springer Series in Chemical Physics. Berlin: Springer-Verlag.
PLAKIDA, N. M., BIELUSHKIN, A. V., NATKANIEC, I. & WASIUTYNSKI, T. (1983). *Phys. Status Solidus B*, 118, 129–133.
PUSIOL, D. J., WOLFENSON, A. E. & BRUNETTI, A. H. (1989). *Phys Rev. B*, 40, 2523–2528.
SAITO, K., KIKUCHI, K. & IKEMOTO, I. (1992). *Solid State Commun.* 81, 241–243.
SHIELDS, K. G. & KENNARD, C. H. L. (1977). *J. Chem. Soc. Perkin Trans* 2, p. 463.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). *The XRAY72 System*, Version of June 1972. Technical Report TR-192. Computer Science Center, Univ. of Maryland, College Park, USA.
TADDEI, G., BONADEO, H., MARZZOCHI, M. P. & CALIFANO, S. (1973). *J. Chem. Phys.* 56, 966–978.
WILLIAMS, D. E. (1967). *J. Chem. Phys.* 47, 4680–4684.
WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* 1, 173–177.
WOLFENSON, A. E., PUSIOL, D. J. & BRUNETTI, A. A. (1990). *Z. Naturforsch. Teil A*, 45, 334–339.
ZÚÑIGA, F. J., PÉREZ-MATO, J. M. & BRECZEWSKI, T. (1993). *Acta Cryst.* B49, 1060–1068.

# Crystal Structures and Photochemistry of Triphenylphosphine Oxide Complexes of Ethyl Hydrogen 9,10-Dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

BY RAY JONES, ZHAOQING LIU, JOHN R. SCHEFFER AND JAMES TROTTER

*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1*

## Abstract

The detailed course of the photochemical rearrangement reactions of dibenzobarrelenedicarboxylates has been studied by crystal structure analyses of two complexes of triphenylphosphine oxide (1) with the monoester ethyl hydrogen 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (2), and by correlation of the crystal structure data with photochemical behaviour. Crystal data: $T = 294$ K, Cu$K\alpha$, $\lambda = 1.54178$ Å. (1.2), $C_{18}H_{15}OP.C_{20}H_{16}O_4$, $M_r = 598.63$, $P\bar{1}$, $a = 13.501$ (1), $b = 14.845$ (1), $c = 8.5190$ (6) Å, $\alpha = 102.21$ (1), $\beta = 98.68$ (1), $\gamma = 68.70$ (1)°, $Z = 2$, $R = 0.039$ for 4546 reflections with $I > 3\sigma(I)$; (1.2).0.5toluene, $C_{18}H_{15}OP.C_{20}H_{16}O_4.0.5C_7H_8$, $M_r = 644.71$, $P2_1/n$, $a = 8.546$ (2), $b = 28.164$ (5), $c = 14.368$ (2) Å, $\beta = 98.81$ (2)°, $Z = 4$, $R = 0.052$ for 3462 reflections. Both crystals contain pairs of molecules linked by O—H$\cdots$O hydrogen bonds, with dimensions and conformations similar to those of previously studied analogues. In the unsolvated crystal the ester group of the monoester is fully conjugated with the C(11)=C(12) double bond [C=C—C=O torsion angle = $-179.6$ (2)°, $\cos^2$(angle) = 1.0], but the acidic group is non-conjugated [109.0 (3)°, 0.11]. In the toluene solvate the opposite is the case, the ester group being non-conjugated [110.5 (5)°, 0.12], and the acid group conjugated [$-13.8$ (6)°, 0.94]. The different amounts of photoproducts formed in the solid-state photolyses can be correlated with these conformational differences.

## Introduction

Triphenylphosphine oxide (1) is a good hydrogen-bond acceptor and forms crystalline complexes with a variety of hydrogen-bond donors (Etter & Baures, 1988). The present paper studies the influence that co-crystallization might have on the photochemical reactivity of the 9,10-ethenoanthracene compound (2). (2) and its derivatives undergo di-$\pi$-methane photorearrangements in a variety of solid and liquid media, to give (3) and (4) [isolated as diesters after diazomethane workup (Gudmundsdottir, Scheffer & Trotter, 1994; Gudmundsdottir, Li, Scheffer, Rettig & Trotter, 1994)]; the ratio in which these photoproducts are formed (and the optical purity of any chiral products) can be correlated with the molecular structure of the reactant, and in particular with the amount of conjugative interaction of the ester and acid

Table 1. *Crystal data, data collection and refinement parameters*

|  | (1.2) | (1.2).0.5toluene |
|---|---|---|
| **Crystal data** | | |
| Formula | $C_{18}H_{15}OP.C_{20}H_{16}O_4$ | $C_{18}H_{15}OP.C_{20}H_{16}O_4.0.5C_7H_8$ |
|  | $= C_{38}H_{31}O_5P$ | $= C_{41.5}H_{35}O_5P$ |
| M.p. (K) | 410–412 | 350–352 |
| $M_r$ | 598.63 | 644.71 |
| Dimensions | $0.4 \times 0.2 \times 0.1$ | $0.35 \times 0.20 \times 0.05$ |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 13.501 (1) | 8.546 (2) |
| $b$ (Å) | 14.845 (1) | 28.164 (5) |
| $c$ (Å) | 8.5190 (6) | 14.368 (2) |
| $\alpha$ (°) | 102.21 (1) | 90 |
| $\beta$ (°) | 98.68 (1) | 98.81 (2) |
| $\gamma$ (°) | 68.70 (1) | 90 |
| $V$ (Å³) | 1549.6 (5) | 3417 (2) |
| $Z$ | 2 | 4 |
| $D_x$ (g cm⁻³) | 1.283 | 1.253 |
| $F(000)$ | 628 | 1356 |
| $\mu$ (cm⁻¹) | 11.2 | 10.5 |

Data collection (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $T = 294$ K)

| | | |
|---|---|---|
| Reflections for cell | | |
| number | 24 | 23 |
| $2\theta$ (°) | 87.5–93.7 | 38.0–76.3 |
| $2\theta_{max}$ (°) | 155 | 155 |
| Scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| $\omega$ scan width (°) | | |
| $a + b\tan\theta$ | | |
| $a$ | 0.89 | 0.94 |
| $b$ | 0.20 | 0.20 |
| Scan speed* (° min⁻¹) | 32.0 | 8.0 |
| $h$ | 0–17 | 0–11 |
| $k$ | −19–19 | 0–36 |
| $l$ | −11–11 | −18–18 |
| Absorption | $\Psi$ scans | $\Psi$ scans |
| Transmission | 0.86–1.0 | 0.73–1.0 |
| Total no. of measured reflections | 6604 | 7722 |
| Total no. of unique reflections | 6328 | 7231 |
| $R_{int}$ | 0.039 | 0.057 |
| Intensity variation | Negligible | 9% decay |
| Reflections $>3\sigma(I)$ | 4546 | 3462 |
| % | 71.8 | 47.9 |
| | | |
| Refinement . | | |
| No. of parameters | 522 | 554 |
| Data/parameters | 8.7 | 6.2 |
| $\Delta/\sigma_{max}$ | 0.03 | 0.1 |
| $\Delta\rho$ (e Å⁻³) | −0.26–0.31 | −0.29–0.33 |
| $R$ | 0.039 | 0.052 |
| $wR$ | 0.041 | 0.048 |
| G.O.F. | 2.55 | 2.77 |
| Extinction ($\times 10^6$) | 4.2 | 1.2 |
| $p$ factor † | 0.00 | 0.00 |

\* Up to eight rescans for reflections with $I < 40\sigma(I)$.

$\dagger \sigma^2(I) = S + 4(B_1 + B_2) + (pI)^2$, where $S$ = scan, $B_1, B_2$ = background counts.

groups with the C=C double bond. Co-crystallization of (1) and (2) from xylene gives crystals of the (1.2) complex, while crystals from toluene (or benzene) contain half a molecule of toluene (or benzene) solvent per (1.2) pair. The (1.2) complex and the toluene solvate have been studied by X-ray methods.

## Experimental

Data, measured on a Rigaku AFC-6S diffractometer, are summarized in Table 1. The structures were solved by direct methods, and refined by full-matrix least-squares procedures, with $w = 1/\sigma^2(F)$. The toluene molecule in the solvated crystals is disordered around a centre of symmetry. The region of the difference map contained several peaks, which could be interpreted and refined in terms of three full-weight and one half-weight C atoms, with several smaller residual peaks; the peaks are probably composite, corresponding to the overlap of several orientations, so that the details of the disordered arrangement are not clear (a possible interpretation is shown in the depository material*). Non-H atoms were refined anisotropically, and H atoms were located from difference syntheses and refined isotropically. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV), computer programs as supplied in *TEXSAN* (MSC, 1989). Details of the refinements are given in Table 1.

## Discussion

Final positional parameters are given in Table 2, selected molecular parameters in Table 3, and other data have been deposited.*

Both crystals contain pairs of (1.2) molecules linked by carboxyl-O—H· · ·O-phosphine hydrogen bonds (Fig. 1, Table 3). The structures and dimensions of the (1) and (2) molecules are very similar to those in the three crystal forms of triphenylphosphine oxide (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970; Ruban & Zabel, 1976; Brock, Schweizer & Dunitz, 1985; Spek, 1987) and in related ethenoanthracenes (*e.g.* Pokkuluri, Scheffer & Trotter, 1993*a,b*). The major difference between the two structures is in the orientations of the substituent ester and acidic groups of (2). In the unsolvated crystals, the ester group is in the plane of the C(11)=C(12) double bond and thus fully conjugated, while the acidic group is rotated 71° out-of-plane, and hence is almost non-conjugated; the relevant C=C—C=O torsion angles are −179.6(2) and 109.0(3)°, respectively, with cos²(angle) (a measure of the amount of conjugative interaction) 1.0 (100%) for the ester group and 0.11 (11%) for the acidic group. In the toluene solvate the opposite is found, with the ester group non-conjugated [110.5(5)°, 12% conjugation], and the acid group conjugated [−13.8(6)°, 94% conjugated]. These differences are also reflected in the C—CO₂R distances (Table 3) of 1.477(3) and 1.497(3) Å for the CO₂Et and CO₂H groups, respectively, in the unsolvated crystals, close to the expected conjugated (1.470 Å) and non-conjugated (1.497 Å) distances (Allen, 1981); for the solvated crystals, the distances are reversed, 1.491 (6) and 1.473 (6) Å.

Table 2. *Positional and equivalent isotropic thermal* ($\text{Å}^2$) *parameters*

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| (1.2) | | | | |
| P(1) | 0.37539 (4) | 0.22740 (4) | 0.36124 (7) | 3.44 (3) |
| O(1) | 0.2730 (2) | 0.4697 (1) | 0.1613 (2) | 5.5 (1) |
| O(2) | 0.2286 (2) | 0.5668 (1) | 0.3941 (2) | 6.4 (1) |
| O(3) | 0.3996 (1) | 0.6043 (1) | 0.1786 (2) | 4.78 (9) |
| O(4) | 0.3702 (1) | 0.7155 (1) | 0.0211 (2) | 5.7 (1) |
| O(5) | 0.3266 (1) | 0.3142 (1) | 0.2799 (2) | 5.0 (1) |
| C(1) | −0.0292 (2) | 0.6027 (2) | −0.1364 (3) | 3.9 (1) |
| C(2) | −0.0438 (2) | 0.5964 (2) | −0.3037 (3) | 4.8 (1) |
| C(3) | 0.0018 (2) | 0.6433 (2) | −0.3789 (3) | 5.2 (2) |
| C(4) | 0.0625 (2) | 0.6979 (2) | −0.2904 (3) | 4.7 (1) |
| C(4A) | 0.0773 (2) | 0.7045 (2) | −0.1255 (3) | 3.6 (1) |
| C(5) | 0.0429 (2) | 0.9288 (2) | 0.1586 (3) | 4.7 (1) |
| C(6) | −0.0285 (2) | 0.9805 (2) | 0.2740 (4) | 5.7 (2) |
| C(7) | −0.0732 (2) | 0.9329 (2) | 0.3481 (3) | 5.6 (2) |
| C(8) | −0.0486 (2) | 0.8318 (2) | 0.3093 (3) | 4.4 (1) |
| C(8A) | 0.0217 (2) | 0.7803 (1) | 0.1926 (2) | 3.5 (1) |
| C(9) | 0.0590 (2) | 0.6700 (1) | 0.1329 (2) | 3.3 (1) |
| C(9A) | 0.0318 (2) | 0.6563 (1) | −0.0492 (2) | 3.3 (1) |
| C(10) | 0.1421 (2) | 0.7587 (2) | −0.0071 (3) | 3.7 (1) |
| C(10A) | 0.0672 (2) | 0.8282 (1) | 0.1165 (3) | 3.7 (1) |
| C(11) | 0.1809 (2) | 0.6346 (1) | 0.1556 (2) | 3.3 (1) |
| C(12) | 0.2245 (2) | 0.6816 (1) | 0.0841 (3) | 3.5 (1) |
| C(13) | 0.2331 (2) | 0.5541 (1) | 0.2528 (3) | 3.5 (1) |
| C(14) | 0.3383 (2) | 0.6696 (2) | 0.0885 (3) | 3.8 (1) |
| C(15) | 0.5132 (2) | 0.5875 (2) | 0.1950 (4) | 5.4 (1) |
| C(16) | 0.5645 (3) | 0.5089 (3) | 0.2935 (6) | 7.7 (2) |
| C(17) | 0.3536 (2) | 0.1211 (1) | 0.2372 (2) | 3.4 (1) |
| C(18) | 0.2496 (2) | 0.1329 (2) | 0.1722 (3) | 4.5 (1) |
| C(19) | 0.2274 (2) | 0.0564 (2) | 0.0684 (3) | 5.5 (2) |
| C(20) | 0.3069 (3) | −0.0324 (2) | 0.0312 (3) | 5.5 (2) |
| C(21) | 0.4092 (2) | −0.0451 (2) | 0.0956 (3) | 5.3 (2) |
| C(22) | 0.4333 (2) | 0.0317 (2) | 0.1981 (3) | 4.3 (1) |
| C(23) | 0.5162 (2) | 0.2021 (1) | 0.4102 (2) | 3.5 (1) |
| C(24) | 0.5668 (2) | 0.2453 (2) | 0.3336 (3) | 5.0 (1) |
| C(25) | 0.6721 (2) | 0.2357 (2) | 0.3773 (4) | 6.1 (2) |
| C(26) | 0.7286 (2) | 0.1828 (2) | 0.4950 (3) | 5.5 (2) |
| C(27) | 0.6813 (2) | 0.1383 (2) | 0.5692 (3) | 5.6 (2) |
| C(28) | 0.5753 (2) | 0.1481 (2) | 0.5282 (3) | 4.8 (1) |
| C(29) | 0.3192 (2) | 0.2447 (2) | 0.5484 (3) | 3.8 (1) |
| C(30) | 0.3307 (2) | 0.1668 (2) | 0.6240 (3) | 4.7 (1) |
| C(31) | 0.2981 (2) | 0.1841 (3) | 0.7772 (4) | 5.8 (2) |
| C(32) | 0.2528 (2) | 0.2784 (3) | 0.8542 (4) | 6.6 (2) |
| C(33) | 0.2362 (2) | 0.3562 (3) | 0.7789 (4) | 6.3 (2) |
| C(34) | 0.2699 (2) | 0.3399 (2) | 0.6255 (3) | 4.8 (1) |
| | | | | |
| (1.2).0.5toluene | | | | |
| P(1) | 0.0297 (1) | 0.02975 (4) | 0.32040 (7) | 3.59 (4) |
| O(1) | 0.2241 (4) | 0.1198 (1) | 0.5212 (2) | 5.2 (1) |
| O(2) | 0.3445 (4) | 0.1623 (1) | 0.4211 (2) | 5.8 (2) |
| O(3) | 0.6627 (3) | 0.2099 (1) | 0.5012 (2) | 5.1 (1) |
| O(4) | 0.5211 (4) | 0.2747 (1) | 0.4590 (3) | 7.9 (2) |
| O(5) | 0.1334 (3) | 0.0556 (1) | 0.3964 (2) | 4.6 (1) |
| C(1) | 0.4009 (6) | 0.1556 (2) | 0.8238 (3) | 5.7 (2) |
| C(2) | 0.5262 (7) | 0.1604 (2) | 0.8969 (3) | 7.1 (3) |
| C(3) | 0.6344 (7) | 0.1965 (2) | 0.8969 (4) | 6.7 (3) |
| C(4) | 0.6234 (5) | 0.2287 (2) | 0.8238 (4) | 5.5 (3) |
| C(4A) | 0.4984 (5) | 0.2246 (1) | 0.7504 (3) | 4.3 (2) |
| C(5) | 0.2393 (6) | 0.3213 (2) | 0.6732 (3) | 5.0 (2) |
| C(6) | 0.0818 (7) | 0.3308 (2) | 0.6806 (4) | 6.1 (3) |
| C(7) | −0.0217 (7) | 0.2939 (2) | 0.6839 (4) | 6.4 (3) |
| C(8) | 0.0270 (5) | 0.2468 (2) | 0.6799 (3) | 5.3 (2) |
| C(8A) | 0.1829 (5) | 0.2379 (1) | 0.6691 (3) | 4.0 (2) |
| C(9) | 0.2588 (5) | 0.1891 (1) | 0.6644 (3) | 4.0 (2) |
| C(9A) | 0.3892 (5) | 0.1877 (1) | 0.7498 (3) | 4.3 (2) |
| C(10) | 0.4578 (5) | 0.2578 (1) | 0.6658 (3) | 4.1 (2) |
| C(10A) | 0.2897 (5) | 0.2751 (1) | 0.6697 (3) | 4.2 (2) |
| C(11) | 0.3424 (4) | 0.1905 (1) | 0.5764 (3) | 3.8 (2) |
| C(12) | 0.4469 (4) | 0.2259 (1) | 0.5786 (3) | 3.8 (2) |
| C(13) | 0.3054 (5) | 0.1564 (1) | 0.4984 (3) | 4.1 (2) |
| C(14) | 0.5442 (5) | 0.2390 (2) | 0.5047 (3) | 4.5 (2) |
| C(15) | 0.7660 (7) | 0.2210 (3) | 0.4301 (4) | 6.7 (3) |

Table 2 (*cont.*)

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| C(16) | 0.8969 (7) | 0.1869 (2) | 0.4448 (5) | 6.3 (3) |
| C(17) | −0.1718 (4) | 0.0265 (1) | 0.3411 (2) | 3.6 (2) |
| C(18) | −0.2586 (6) | 0.0679 (2) | 0.3372 (3) | 4.9 (2) |
| C(19) | −0.4106 (6) | 0.0679 (2) | 0.3597 (4) | 5.6 (3) |
| C(20) | −0.4774 (6) | 0.0266 (2) | 0.3820 (3) | 5.8 (3) |
| C(21) | −0.3945 (6) | −0.0151 (2) | 0.3853 (4) | 5.9 (3) |
| C(22) | −0.2414 (6) | −0.0157 (2) | 0.3640 (3) | 4.7 (2) |
| C(23) | 0.0986 (4) | −0.0299 (1) | 0.3099 (3) | 3.6 (2) |
| C(24) | 0.1794 (6) | −0.0513 (2) | 0.3879 (3) | 5.0 (2) |
| C(25) | 0.2398 (6) | −0.0963 (2) | 0.3864 (4) | 5.6 (3) |
| C(26) | 0.2192 (6) | −0.1208 (2) | 0.3041 (4) | 6.1 (3) |
| C(27) | 0.137 (1) | −0.1006 (2) | 0.2262 (4) | 9.7 (4) |
| C(28) | 0.0772 (8) | −0.0553 (2) | 0.2276 (4) | 7.8 (3) |
| C(29) | 0.0237 (4) | 0.0593 (1) | 0.2089 (3) | 3.8 (2) |
| C(30) | 0.1360 (5) | 0.0939 (2) | 0.2008 (4) | 5.2 (2) |
| C(31) | 0.1334 (7) | 0.1178 (2) | 0.1159 (4) | 6.3 (3) |
| C(32) | 0.0192 (8) | 0.1075 (2) | 0.0409 (4) | 7.0 (3) |
| C(33) | −0.0932 (7) | 0.0736 (2) | 0.0480 (4) | 6.1 (3) |
| C(34) | −0.0915 (5) | 0.0498 (2) | 0.1323 (3) | 4.8 (2) |

Table 3. *Selected bond lengths* (Å) *and angles* (°)

| | (1.2) | (1.2).0.5toluene |
|---|---|---|
| P=O | 1.483 (2) | 1.487 (3) |
| P—C | 1.798–1.800 (2) | 1.794–1.799 (4) |
| O=P—C | 110.8–112.2 (1) | 110.7–112.5 (2) |
| C—P—C | 106.1–109.5 (1) | 105.9–108.9 (2) |
| | | |
| C(11)=C(12) | 1.337 (4) | 1.338 (5) |
| C(12)—CO$_2$Et | 1.477 (3) | 1.491 (6) |
| C(11)—CO$_2$H | 1.497 (3) | 1.473 (6) |
| Hydrogen bonds | | |
| O···O | 2.534 (3) | 2.581 (4) |
| O—H | 1.00 (4) | 1.01 (5) |
| H···O | 1.55 (4) | 1.58 (5) |
| O—H···O | 165 | 168 |

*Photochemistry*

The accepted mechanism for the di-$\pi$-methane photochemical reaction in ethenoanthracenes involves initial vinyl-benzo carbon–carbon bond formation (Zimmerman, Sulzbach & Tollefson, 1993); in an asymmetrical reactant such as (2), two pathways are possible (path *a*



(1)  (2)

$Ph_3P=O.$

*hv*

(3)
(path *a*)

+

(4)
(path *b*)

(I)

and path *b*), leading to two isomeric products, (3) and (4) (Borecka, Fu, Gudmundsdottir, Jones, Liu, Scheffer & Trotter, 1994). The more favourable pathway involves bonding at the C atom to which the less-conjugated carboxyl substituent is attached, since this stabilizes the resulting radical by electron delocalization over the more conjugated substituent. Thus, in crystals of (1.2), with a
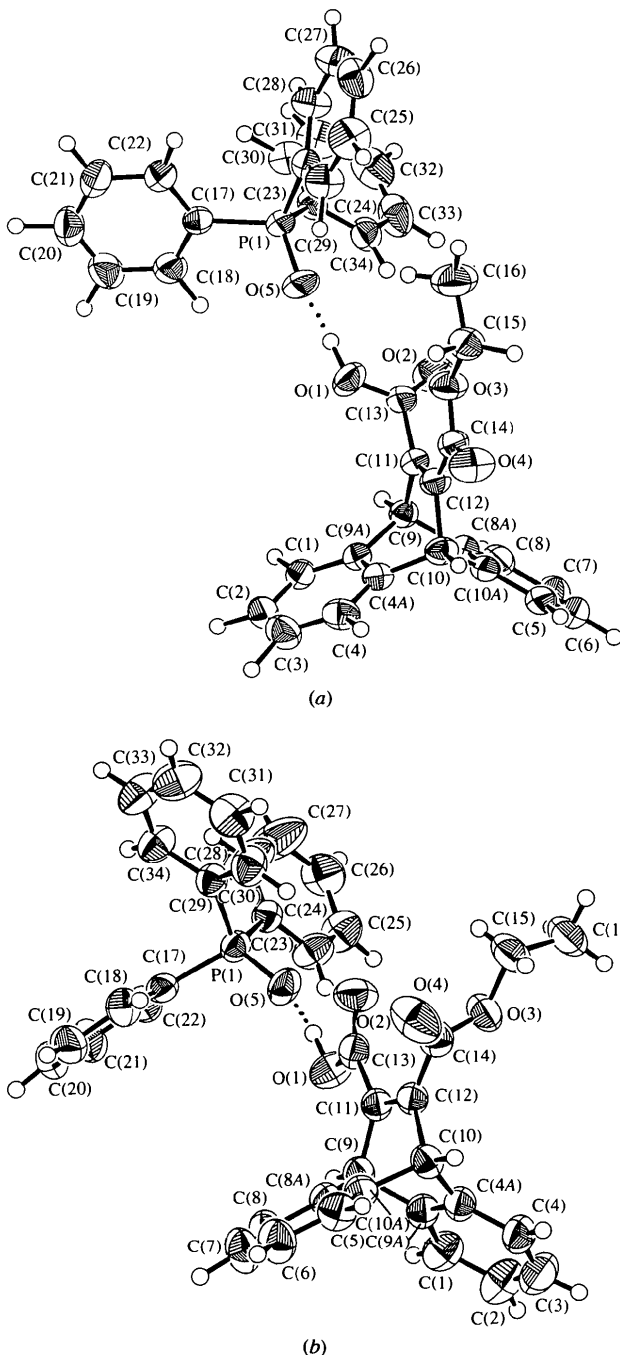
Table 4. *Photochemical parameters*

|  | (2) | (1.2) | (1.2).0.5toluene |
|---|---|---|---|
| M.p. (K) | 493–494 | 410–412 | 350–352 |
| (3):(4) ratio (solid state) | 0:100 [0:100]* | 56:44 | 3:97 |
| C=C—C=O (ester) | [+65.6 (3)] | −179.6 (2) | +110.5 (5) |
| % conjugation | [17] | 100 | 12 |
| C=C—C=O (acid) | [−164.4 (3)] | +109.0 (3) | −13.8 (6) |
| % conjugation | [93] | 11 | 94 |

\* Values in square brackets are for the $CO_2^iPr/CO_2H$ compound (Pokkuluri & Trotter, 1994); crystals of (2) suitable for X-ray work could not be obtained.

conjugated ester substituent, path *a* should be more favourable, resulting in preferential formation of photoproduct (3); this is as observed (Table 4), although only in a [(3):(4)] ratio of 56:44. Conversely in (1.2).0.5toluene, which exhibits a conjugated acid substituent, path *b* and the formation of (4) is preferred, again as observed [(3):(4) = 3:97]. Photolysis of crystals of the free acid (2) produces only (4); although the crystal structure of (2) has not been determined, data for the analogous isopropyl derivative (Pokkuluri & Trotter, 1994) indicate conjugation of the acid group and hence prediction of path *b* and the formation of (4), as observed (Table 4).

The photolysis reactions are also often influenced by intermolecular interactions (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990), since large movement of a substituent is involved during the initial carbon–carbon bond formation. In the present complexes, initial bridging that involves movement of the $CO_2H$ group [path *a*, formation of (3)] is likely to be disfavoured, since it would disrupt the hydrogen bonding (Garcia-Garibay, Scheffer & Watson, 1992). This reinforces the conjugation effect in (2) and (1.2).0.5toluene, accounting for the nearly 100% production of (4), but opposes it in (1.2), thus accounting for the lower regioselectivity (only 56:44) in the photolysis of the (1.2) crystals.

Fig. 1. The dibenzobarrelene/phosphine oxide pairs in (*a*) (1.2) and (*b*) (1.2).0.5toluene; 50% thermal probability ellipsoids.

**References**

ALLEN, F. H. (1981). *Acta Cryst.* **B37**, 890–900.
BANDOLI, G., BORTOLOZZO, G., CLEMENTE, D. A., CROATTO, U. & PANATTONI, C. (1970). *J. Chem. Soc. A*, pp. 2778–2780.
BORECKA, B., FU, T. Y., GUDMUNDSDOTTIR, A. D., JONES, R., LIU, Z., SCHEFFER, J. R. & TROTTER, J. (1994). *Chem. Mater.* **6**, 1094–1095.
BROCK, C. P., SCHWEIZER, W. B. & DUNITZ, J. D. (1985). *J. Am. Chem. Soc.* **107**, 6964–6970.
ETTER, M. C. & BAURES, P. W. (1988). *J. Am. Chem. Soc.* **110**, 639–640.
GARCIA-GARIBAY, M., SCHEFFER, J. R., TROTTER, J. & WIREKO, F. C. (1990). *Acta Cryst.* **B46**, 79–87.
GARCIA-GARIBAY, M. A., SCHEFFER, J. R. & WATSON, D. G. (1992). *J. Org. Chem.* **57**, 241–247.
GUDMUNDSDOTTIR, A. D., LI, W., SCHEFFER, J. R., RETTIG, S. & TROTTER, J. (1994). *Mol. Cryst. Liq. Cryst.* **240**, 81–88.
GUDMUNDSDOTTIR, A. D., SCHEFFER, J. R. & TROTTER, J. (1994). *Tetrahedron Lett.* **35**, 1397–1400.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands TX 77381, USA.

POKKULURI, P. R. & TROTTER, J. (1994). *Acta Cryst.* C50, 922–924.

POKKULURI, P. R., SCHEFFER, J. R. & TROTTER, J. (1993a). *Acta Cryst.* B49, 107–116.

POKKULURI, P. R., SCHEFFER, J. R. & TROTTER, J. (1993b). *Acta Cryst.* B49, 754–760.

RUBAN, G. & ZABEL, V. (1976). *Cryst. Struct. Commun.* 5, 671–677.

SPEK, A. L. (1987). *Acta Cryst.* C43, 1233–1235.

ZIMMERMAN, H. E., SULZBACH, H. M. & TOLLEFSON, M. B. (1993). *J. Am. Chem. Soc.* 115, 6548–6556.

# SHORT COMMUNICATION

## Experimental and theoretical determination of electronic properties in L-dopa. Erratum.

By S. T. HOWARD, M. B. HURSTHOUSE and C. W. LEHMANN, *School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, Cardiff CF1 3TB, Wales,* and E. A. POYNER, *Pharmaceutical Science Institute, Aston University, Aston Triangle, Birmingham B4 7ET, England*

### Abstract

The reference number in the deposit footnote on p. 330 [Howard, Hursthouse, Lehmann & Poyner (1995). *Acta Cryst.* B51, 328–337] was incorrectly quoted as SE0154. The correct reference number is CR0467.

All relevant information is given in the *Abstract*.

# Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (R. F. Bryan, Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, Virginia 22901, USA). As far as practicable, books will be reviewed in a country different from that of publication.*

## Highlights of chemistry as mirrored in Helvetica Chimica Acta.

Edited by M. V. KISAKUREK and E. HEILBRONNER. Pp. v + 985. Basel: Verlag Helvetica Chimica Acta and Weinheim: VCH Verlagsgesellschaft mbH, 1994. Price DM 248. ISBN 1-906390-08-X.

In the highly charged atmosphere of nationalism accompanying the first world war, chemists in neutral Switzerland faced a problem. Accustomed to publishing their work in the chemical journals of their larger neighbors, chemists who, before the war would have made their choice of journal solely on the basis of linguistic convenience or the desire to reach as wide an audience as possible through the use of the German language, the *lingua franca* of the chemical world of the day, hesitated, during wartime, to make choices that might be interpreted as gestures of moral or even material support for one or other of the combatant nations. And, of course, no matter which journal was chosen, the potential audience was greatly reduced. The Swiss Chemical Society, with some help from its friends in industry, resolved this issue by deciding to publish its own journal, neatly finessing the question of language parity by giving it the latinized title *Helvetica Chimica Acta*. To further emphasize Swiss neutrality, only contributions from Swiss laboratories were initially accepted. The story of the founding of the journal and its subsequent editorial history are entertai-

ningly and informatively described by Edgar Heilbronner and Volkan Kisakürek in their introduction to this delightful volume, issued to commemorate *Helvetica*'s 75th anniversary.

The main body of the book is a series of charmingly subjective and necessarily idiosyncratic historical reviews of selected areas of chemistry as they have developed in articles in the journal over the first 75 years of its existence. Here are: Venanzi on coordination chemistry; Heimgartner and Hansen on structure and mechanisms in organic chemistry and, later, on organic photochemistry; Guggisberg and Hesse on alkaloid research; Eugster on carotinoid chemistry; Ohloff on flavor and perfume chemistry (a particularly Swiss strength occupying the attention of most of the giants); Zollinger on color chemistry; Tamm on carbohydrates, plant and microbial substances; Kalvoda on steroids; chemists from Hoffmann–La Roche on vitamins; Woggon on triterpenes; Günthard and Heilbronner on physical chemistry; Bürgi and Dunitz on structural chemistry. A rich feast, indeed!

Vladimir Prelog, in his introductory preface, declines the invidious task of identifying individual landmark contributions, leaving that choice to the reader. Your reviewer is no more anxious than he to play that game. Like Professor Prelog, I simply observe that many major contributions are highlighted, as are many meritorious lesser ones. To be mentioned at all in a work of this kind always produces a warm feeling (and, presumably, not to be mentioned produces a converse one!). I was, therefore, pleased to find my own modest contribution to