The Crystal and Molecular Structure of 1,1'-Bisisopropoxycarbonyl-9,9'-bisfluorenylidene

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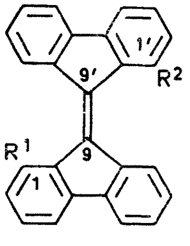
Summary The crystal structure of the title compound confirms that the molecule has a *trans*-configuration in the solid state and shows that it adopts a twisted conformation rather than the folded conformation reported for the unsubstituted bisfluorenylidene.

THE results of recent temperature-dependent n.m.r. studies[1] on the inversion and *cis–trans*-interconversion rates of a series of 1,1'-disubstituted 9,9'-bisfluorenylidenes (Ia—c) can be interpreted on the basis that the major conformer in solution has the *trans*-configuration and that (Ia) and (Ib) retain this configuration in the solid state whereas (Ic) appears to possess a *cis*-configuration in the solid state which is that of a minor conformer in solution. The *cis*- and *trans*-configurations of the twisted and folded conformations of (I) are conveniently represented by the Newman projections (II). A three-dimensional *X*-ray investigation of the bisisopropoxycarbonyl derivative (Ia) has been undertaken as part of a continuing study of the solid-state structures of this series of molecules.

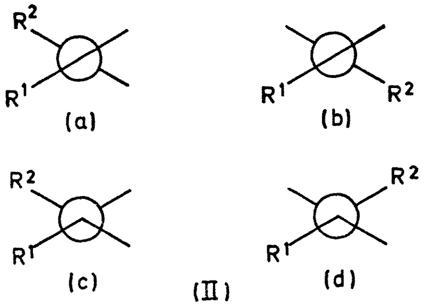
Crystals were obtained from acetone as red needles. *Crystal data:* $C_{34}O_4H_{28}$, $M = 500{\cdot}6$, monoclinic, $a = 40{\cdot}11$, $b = 8{\cdot}03$, $c = 23{\cdot}79$ Å, $\beta = 91°42'$, $U = 7659$ Å^3, $D_m = 1{\cdot}30$, $Z = 12$, $D_c = 1{\cdot}30$, $F(000) = 3168$, space group is $I2/c$ or Ic (non-standard settings of $C2/c$ and Cc, respectively).



(I) a; $R^1 = R^2 = CO_2Pr^i$
b; $R^1 = CO_2Pr^i$, $R^2 = CO_2Me$
c; $R^1 = R^2 = CO_2Me$
d; $R^1 = R^2 = H$

Three-dimensional data were collected photographically using equi-inclination Weissenberg geometry and were estimated visually; the usual corrections were applied. The 3019 independent reflexions thus obtained were scaled together using 619 reflexions previously recorded on a

Hilger and Watts 4-circle diffractometer. The structure was solved by direct methods, assuming space group $I2/c$ (later confirmed) and refined by block-diagonal, least-squares, and difference Fourier methods to a current $R = 0{\cdot}133$, all atoms being allowed individual isotropic thermal parameters.



(II)

The structure shows that eight molecules lie in general positions in the unit cell and that the remaining four molecules lie in special positions across the crystallographic C_2 axis which is perpendicular to the 9–9′ bond. The Figure shows the general molecule—the special molecule has substantially the same structure. Individual bond lengths and angles are close to expected values but the conformations of both molecules are of the *trans* twisted type (IIb)—both enantiomers being present in the lattice—rather than of the folded conformation as reported for the unsubstituted bisfluorenylidene (Id).[2] The atoms of each of the three independent fluorenylidene fragments are approxomately coplanar (r.m.s. deviations vary from 0·03 to 0·10 Å) and the angles between the mean planes in the two molecules are 49 and 54°; the local torsion angles across the formal double bond (of length 1·39 Å in both molecules) are 39 and 41°, indicating a partial di-radical character for the bond.

The overall conformations of the two crystallographically independent molecules are very similar, the only significant differences being concerned with the orientations adopted by the isopropoxycarbonyl substituents with respect to the bisfluorenylidene framework.

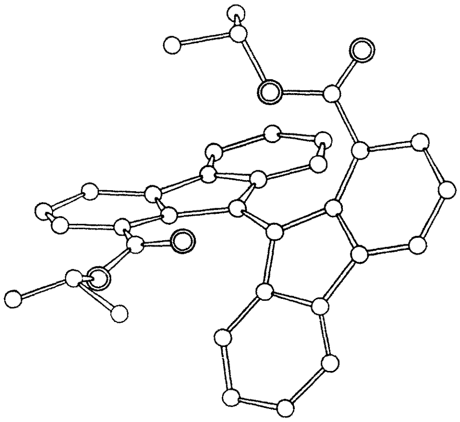


FIGURE. *The molecular structure of the general molecule of* 1,1′-*bisisopropoxycarbonyl*-9,9′-*bisfluorenylidene*; *the oxygen atoms are shown as double circles.*

In view of the results of this analysis, some doubt must arise concerning the structure of the unsubstituted bisfluorenylidene (Id). Preliminary work has demonstrated the inadequacy of the very limited data used in the earlier investigation and initial work by the present authors throws doubt on the accuracy of the reported structure. A re-investigation of this structure is now at an advanced stage.

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[1] I. R. Gault, W. D. Ollis, and I. O. Sutherland, *Chem. Comm.*, 1970, 269.

[2] C. P. Fenimore, *Acta Cryst.*, 1948, **1**, 295; S. C. Nyburg, *ibid.*, 1954, **7**, 779.