

Photodimers of Isobenzofuran: a Novel Application of Lanthanide Induced Shift Spectroscopy to Determine Stereochemistry

Ronald N. Warrener,^{*a} Ian G. Pitt,^a and Richard A. Russell^{*b}

^a Department of Chemistry, The Faculties, Australian National University, P.O. Box 4, Canberra, A.C.T., 2600 Australia

^b Department of Chemistry, Faculty of Military Studies, University of New South Wales, Canberra, A.C.T., 2600 Australia

In acetone solution u.v. irradiation of isobenzofuran at $-60\text{ }^{\circ}\text{C}$ forms an $[8 + 8]$ dimer shown by lanthanide induced shift spectroscopy to have the *anti*-stereochemistry; in ether solution an $[8 + 4]$ dimer is obtained together with a skeletally modified dimer, the structure of which is confirmed by synthesis.

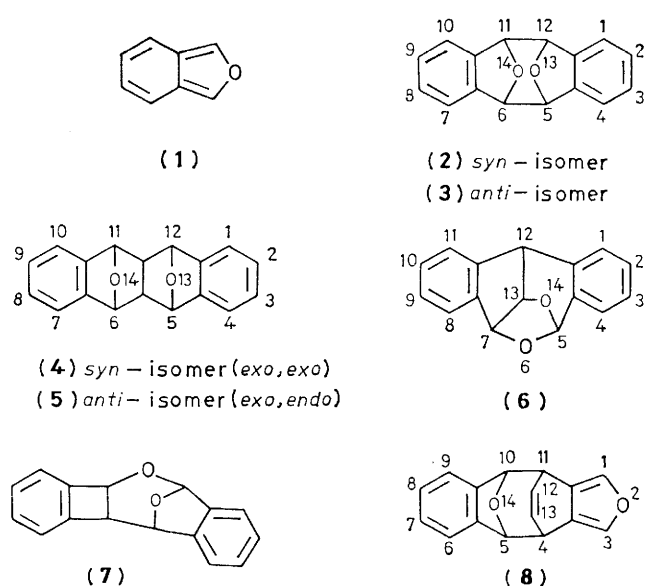
Some years ago we described the isolation of isobenzofuran (1), a highly reactive but isolable crystalline material.¹ The thermal chemistry of isobenzofurans has recently attracted much attention; however photochemical studies have been restricted to the 1,3-diaryl derivatives.² We now report on the solution photochemistry of the parent isobenzofuran.

Irradiation[†] of degassed solutions of isobenzofuran in acetone at $-60\text{ }^{\circ}\text{C}$ led to the formation of a crystalline dimeric product, m.p. $234\text{--}236\text{ }^{\circ}\text{C}$, (dimer A).[‡] ¹H N.m.r. spectroscopy[§] supported the formation of a symmetrical product consistent with either the *syn*- $[8 + 8]$ dimer (2) or the

[†] Freshly prepared isobenzofuran was transferred to a cooled quartz tube under vacuum. Acetone was distilled (*in vacuo*) into the tube at liquid nitrogen temperature and the solution repeatedly freeze-thaw degassed. The resulting solution at $-60\text{ }^{\circ}\text{C}$ was photolysed through a Vycor filter with an American Hanovia medium pressure mercury arc lamp (450 W).

[‡] All new compounds gave satisfactory i.r., mass spectral, and microanalytical data.

[§] Dimer A (5,6,11,12-tetrahydro-5,12:6,11-diepoxydibenzo[*a,e*]cyclo-octene): ¹H n.m.r. δ 4.79 (4H, s, aliphatic) and 7.34 (8H, s, aromatic). Dimer B (7,12-dihydro-5,7,12-epoxymetheno-5*H*-dibenz[*c,f*]oxocin): ¹H n.m.r. δ 4.55 (1H, d, *J* 6.5 Hz, 12-H), 5.10 (1H, d, *J* 4.5 Hz, 7-H), 5.54 (1H, dd, *J* 4.5, 6.5 Hz, 13-H), 6.18 (1H, s, 5-H), and 7.1–7.5 (8H, m, aromatic); ¹³C n.m.r. (aliphatics only) δ 46.96 (d, *J* 137.9 Hz, C-12), 80.48 (d, *J* 160 Hz, C-13), 81.64 (d, *J* 159.6 Hz, C-7), and 103.85 p.p.m. (d, *J* 172.9 Hz, C-5). Dimer C (4,5,10,11-tetrahydro-5,10-epoxy-4,11-ethenobenzo[5,6]cyclo-octa[1,2-*c'*]furan): ¹H n.m.r. δ 3.73 (2H, ddd, *J* 3.1, 4.9, 6.3 Hz, 4,11-H), 5.01 (2H, d, *J* 6.3 Hz, 5,10-H), 5.88 (2H, dd, *J* 3.1, 4.9 Hz, 12,13-H), and 7.20 (6H, s, aromatic).



anti- $[8 + 8]$ dimer (3). A distinction between these two forms was achieved by the application of a lanthanide induced shift spectroscopy (i.s.s.) technique described recently.³ We first established that compounds containing two structurally confined and *syn*-related ether oxygen atoms, e.g. (4)⁴ act as bidentate ligands and form tightly bound 1:1 complexes

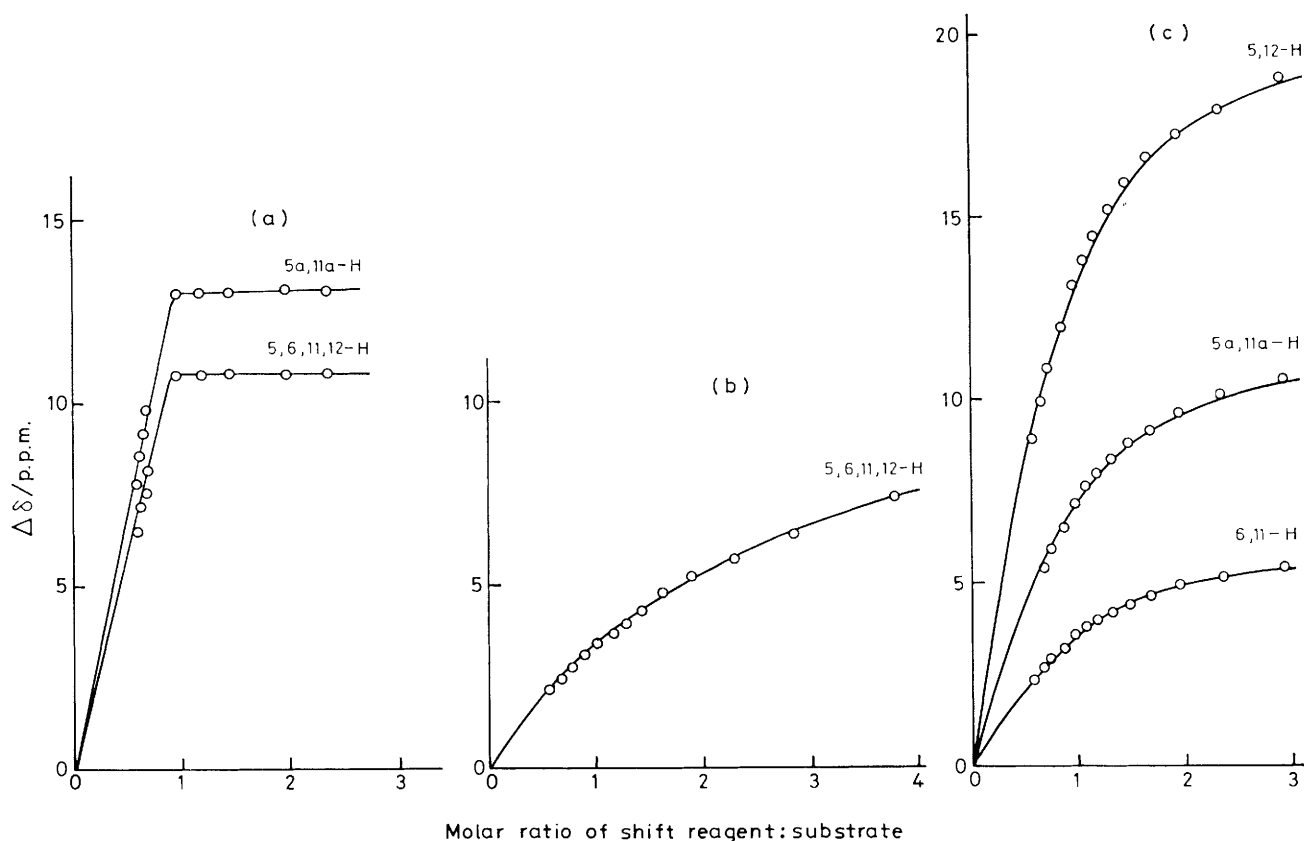
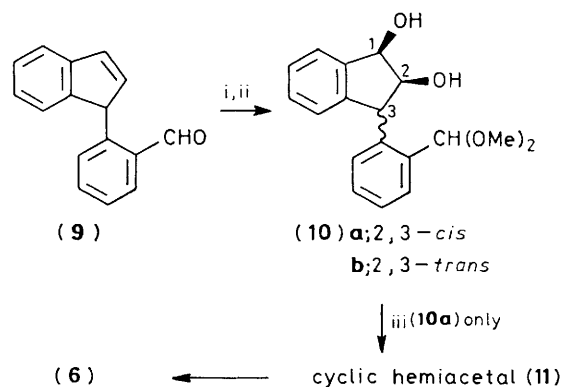


Figure 1. Lanthanide induced chemical shift profiles: (a) model for *syn*-stereochemistry (**4**), (b) isobenzofuran dimer A, (c) model for *anti*-stereochemistry (**5**).

upon treatment with the shift reagent $\text{Eu}(\text{fod})_3$ ($\text{fod} = 6,6,7,7,8,8\text{-heptafluoro-2,2-dimethyloctane-3,5-dionato}$).[¶] This is reflected in the sharp discontinuity of the linear l.i.s. chemical shift profile of (**4**) above equimolar ratios [Figure 1(a)]. In contrast the related model for *anti*-stereochemistry (**5**) formed a loosely associated complex which gave a smooth non-linear l.i.s. chemical shift profile [Figure 1(c)]. The *anti*-configuration (**3**) was thus assigned to dimer A since it showed similar l.i.s. characteristics [Figure 1(b)] to those observed for (**5**).

Irradiation of isobenzofuran in degassed ether solution at -60°C yielded two new dimeric products (dimers B and C) together with small amounts of phthalaldehyde.** Dimer B, m.p. $130\text{--}131^\circ\text{C}$, was an unsymmetrical molecule with spectral features[§] consistent with either structure (**6**) or (**7**). A distinction between these two structures became possible after the unambiguous synthesis of (**6**) had been achieved (Scheme 1). Thus hydroxylation of the substituted indene (**9**)⁵ afforded a mixture of *cis*-diols, the major component of which was assigned the 2,3-*trans*-stereochemistry (**10b**) and would not cyclise to an internal acetal. The minor 2,3-*cis*-isomer (**10a**) however, readily eliminated methanol under acid catalysis to yield a crystalline hemiacetal (**11**) which,



Scheme 1. Reagents: i, $\text{MeOH-}p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H-4 \AA sieves}$; ii, $\text{OsO}_4\text{-pyridine}$; iii, H_3O^+ .

when further treated with sulphuric acid in tetrahydrofuran, yielded a product indistinguishable from photodimer B.

Dimer C was only obtained in trace amounts and tentatively ascribed the [8 + 4] structure (**8**) (stereochemistry undefined) on the basis of ^1H n.m.r. spectroscopy[§] and catalytic hydrogenation which yielded a hexahydro-derivative (retaining C_2 symmetry). This structure is novel since it constitutes the first example of cycloaddition occurring in the carbocyclic ring of an isobenzofuran.

These results show that the parent isobenzofuran undergoes all the photoreactions reported for the 1,3-diphenyl derivative and also some which are new. It is interesting that no evidence for the formation of oxatricyclo[4.3.0.0^{7,9}]nona-1,3,5-triene

[¶] Compound (**4**) is considered to be a fair model since the orbital alignments of the oxygen atom lone pairs are essentially the same in each compound, and the oxygen atoms are separated by comparable distances (2.3 vs. 2.7 Å as estimated from Dreiding models).

** Phthalaldehyde is presumed to arise from the addition of traces of oxygen to isobenzofuran but this remains to be proved.

(Dewar isobenzofuran) was obtained although this ring-system has been reported, albeit in heavily substituted form.⁶ In this respect a clear differentiation is observed between isobenzofuran and the 2,2-dialkylated isoindenes where the intramolecular [2 + 2] valence isomerisation dominates the photochemistry.⁷

We thank Dr. I. D. Rae for drawing the Lindoy work to our attention, and Professor D. N. Butler for his interest and advice during the course of this programme.

Received, 18th June 1982; Com. 691

References

- 1 R. N. Warrener, *J. Am. Chem. Soc.*, 1971, **93**, 2346.
 - 2 A. Guyot and J. Catel, *Bull. Soc. Chim. Fr.*, 1906, **35**, 1124; G. Rio and M.-J. Rio, *J. Chem. Soc., Chem. Commun.*, 1982, 72.
 - 3 L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, 1975, **97**, 2275.
 - 4 L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, 1965, **43**, 1559.
 - 5 S. J. Cristol, A. A. Roberts, and T. E. McEntee, *J. Org. Chem.*, 1974, **39**, 829.
 - 6 F. Toda, N. Dan, K. Tanaka, and Y. Takehira, *J. Am. Chem. Soc.*, 1977, **99**, 4529.
 - 7 W. R. Dolbier, K. Matsui, H. J. Dewey, D. V. Horak, and J. Michl, *J. Am. Chem. Soc.*, 1979, **101**, 2136; F. J. Palensky and H. A. Morrison, *J. Am. Chem. Soc.*, 1977, **99**, 3507.
-