tion von (1*b*) bzw. (2*b*) wurden 1911 bzw. 2248 Friedel-Reflexenpaare ausgewertet. Der Ursprung für Verbindung (2*b*) wurde nach der Methode von Flack & Schwarzenbach (1988) festgelegt.

Beide Verbindungen, Datensammlung: *Kuma KM-4 Software* (Kuma Diffraction, 1991); Zellverfeinerung: *Kuma KM-4 Software*; Datenreduktion: *Kuma KM-4 Software*; Lösung der Strukturen: *SHELXS*97 (Sheldrick, 1997*b*); Verfeinerung der Strukturen: *SHELXL*97 (Sheldrick, 1997*a*). Molekülgrafik: *ORTEP*II (Johnson, 1976) und *PLUTO* (Motherwell & Clegg, 1978). Beide Verbindungen, Programm für die Herstellung von Veröffentlichungsmaterialen: *SHELXL*97.

Ich danke Dr E. Linkowska und Dr L. Zaprutko für die Überlassung der untersuchten Verbindungen.

Literatur

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Aono, T., Bieri, J. H., Hesse, M., Kostova, K., Lorenzi-Riatsch, A., Nakashita, Y. & Prewo, R. (1985). *Helv. Chim. Acta*, **68**, 1033–1053.

Brough, P. A., Gallagher, T., Thomas, P., Wonnacott, S., Baker, R., Malik, K. M. A. & Hursthouse, M. B. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1087–1089.

Duax, W. L. & Norton, D. A. (1975). In *Atlas of Steroid Structures*. New York: Plenum Press.

Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.

Florencio, F., Smith-Verdier, P. & Garcia-Blanco, S. (1977). *Cryst. Struct. Commun.* **6**, 561–564.

Govardhan, C., Reddy, R. P., Ramaiah, T. S. & Rao, T. V. (1983). *J. Indian Chem. Soc.* pp. 858–860.

Gzella, A., Linkowska, E., Zaprutko, L. & Wrzeciono, U. (1999). *Acta Cryst.* C**55**, 1031–1034.

Gzella, A., Zaprutko, L., Wrzeciono, U. & Gdaniec, M. (1986). *Acta Cryst.* C**42**, 1859–1862.

Gzella, A., Zaprutko, L., Wrzeciono, U. & Jaskólski, M. (1987). *Acta Cryst.* C**43**, 759–762.

Hufford, C. D., Oguntimein, B. O., Van Engen, D., Muthard, D. & Clardy, J. (1980). *J. Am. Chem. Soc.* **102**, 7365–7367.

Johnson, C. K. (1976). *ORTEP*II. Bericht ORNL-5138. Oak Ridge National Laboratory, Tennessee, VStA.

Kuma Diffraction (1991). *Kuma KM-4 User's Guide*. Kuma Diffraction, Wrocław, Polen.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Universität Cambridge, England.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ruzicka, L., Frame, F. G., Leicester, H. M., Liguori, M. & Brüngger, H. (1934). *Helv. Chim. Acta*, **17**, 426–442.

Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. Universität Göttingen, Deutschland.

Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. Universität Göttingen, Deutschland.

Wajsman, E., Grabowski, M. J., Stepien, A. & Cygler, M. (1978). *Cryst. Struct. Commun.* **7**, 259–262.

Zaprutko, L. (1999). *Pol. J. Chem.* **73**, 333–338.

Novel compounds from 1,2-indanedione and 3,5-dimethoxyaniline

Bruce Taylor, Patrick J. Carroll and Madeleine M. Joullié

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA. E-mail: mjoullie@sas.upenn.edu

Abstract

The reaction of 1,2-indanedione with 3,5-dimethoxyaniline was found to give several products. The initial mode of addition is thought to result from attack of nitrogen at the C2 position of 1,2-indanedione to generate an enamine, which can then undergo subsequent reactions producing 2,2'-bis(3,5-dimethoxyphenylamino)[3,3'-biindene]-1,1'-dione, $C_{34}H_{28}N_2O_6$, and two diastereomers of 11a'-[2-(3,5-dimethoxyphenylamino)-1-oxoinden-3-yl]-6',6a',11',11a'-tetrahydro-1',3'-dimethoxyspiro[indene-2(3*H*),6'-5'*H*-indeno[1,2-*c*]-quinoline]-1,11'-dione as the dichloromethane solvate, $2C_{43}H_{34}N_2O_7 \cdot 2CH_2Cl_2$. X-ray crystal structures have been obtained for these three major products.

Comment

Recently, 1,2-indanediones have been recognized as useful amino acid/amine reagents (Hauze *et al.*, 1998). The nature of the chromophore/fluorophore is not known and there is scant information in the literature regarding these reactions. Ninhydrin, on the other hand, has been investigated in great detail and, as much of the chemistry concerning ninhydrin relates directly to 1,2-indanediones, we thought that some of the reactions involving ninhydrin should be repeated with 1,2-indanediones.

Reactions involving ninhydrin and electron-rich anilines have been reported (Black *et al.*, 1994; Bullington & Dodd, 1993; Friedman, 1967; Shapiro & Chatterjie, 1970). These investigations have found that the products are highly dependent on both the aniline and the conditions employed. From these reactions, several possible products may be formed, as ninhydrin possesses multiple electrophilic sites and the anilines, in many cases, possess several nucleophilic sites. As a result, much debate has taken place as to the regiochemistry of these compounds (Bullington & Dodd, 1993; Shapiro & Chatterjie, 1970). These investigations prompted us to examine the reaction of 1,2-indanedione and 3,5-dimethoxyaniline. In this reaction, the chief mode of addition was reported to occur through the activated

ortho-position of the aniline. Cyclization then occurred producing the indenoindole after reduction. Regiochemistry was assigned unambiguously by X-ray crystallographic analysis of the reduction product (Black *et al.*, 1994).

In contrast with results observed for ninhydrin, we have ascertained that, in anhydrous benzene, it is the nitrogen rather than the activated aniline ring that attacks the 2-position of 1,2-indanedione, giving rise to three major products, namely 2,2'-bis(3,5-dimethoxy-phenylamino)[3,3'-biindene]-1,1'-dione, (2), and two diastereomers of 11a'-[2-(3,5-dimethoxyphenylamino)-1-oxoinden-3-yl]-6',6a',11',11a'-tetrahydro-1',3'-dimethoxy-spiro[indene-2(3*H*),6'-5'*H*-indeno[1,2-*c*]quinoline]-1,11'-dione, (3) and (4). None of the corresponding indeno-indole resulting from cyclization to the C1 position of the 1,2-indanedione was observed.
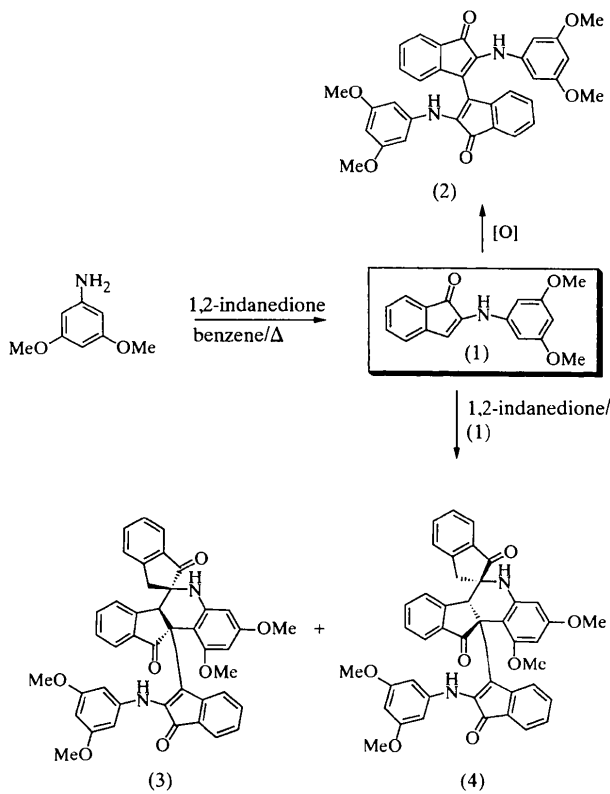
H32) and the neighboring carbonyl O atoms (O9 and O30). The H11···O9 distance is 2.33 (2) Å and the N11—H11···O9 angle is 112 (1)°, while the H32···O30 distance is 2.37 (3) Å and the N32—H32···O30 angle is 109 (2)°. There are no other remarkable intra- or intermolecular contacts.
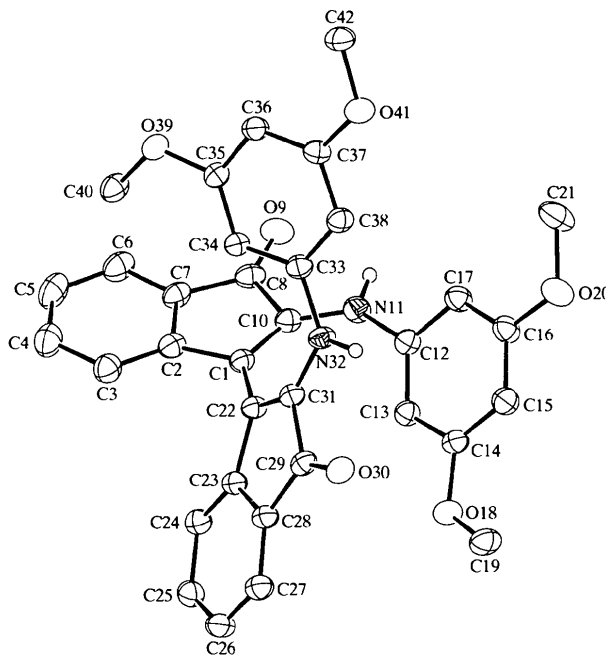

Fig. 1. The molecular structure of compound (2) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Compound (2) is most probably formed after oxidative coupling of the uncharacterized enamine (1), whereas diastereomers (3) and (4) are most likely formed after reaction of enamine (1) with the 1,2-indanedione present, followed by reaction with another equivalent of enamine.

An analysis of the atom–atom contacts indicates that compound (2) participates in intramolecular hydrogen bonding between the two amine H atoms (H11 and

Compounds (3) and (4) are enantiomers but are not related by crystallographic symmetry [there is an approximate center of symmetry at about $(0, 0.57, \frac{1}{4})$]. The configurations around the chiral C atoms in (3) are C9*R*, C10*R* and C18*S*; in (4), the configurations are C9*S*, C10*S* and C18*R*. The conformations of the two molecules are not quite the same (see Table 1); if the two molecules were mirror images, the pairs of torsion angles would differ only in sign.

There are minor differences in the relative orientations of the planar moieties defined by (*a*) C18–C20, C24–C27, (*b*) C18, C32–C40, N42 and (*c*) N42, C43–C48. The torsion angles relating to these structural subunits differ by less than 4° in the two molecules. The dihedral angles between the three planar subunits are also similar: (*a*)–(*b*) 88.9 (1) and 84.5 (1)°, (*a*)–(*c*) 131.2 (1) and 125.8 (1)°, and (*b*)–(*c*) 61.7 (1) and 63.8 (1)°, for (3) and (4), respectively. There are, however, major differences in the orientations of the O28—C29 and O51—C52 methoxy groups and these are the

major structural factors that cause these two chemically enantiomeric molecules to be crystallographically diastereomeric.
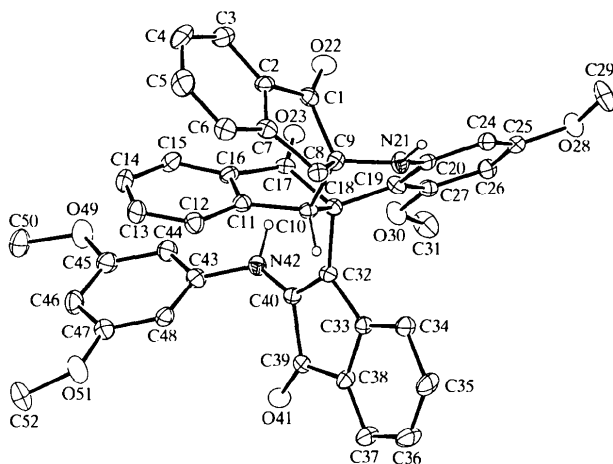

Fig. 2. The molecular structure of compound (3) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.
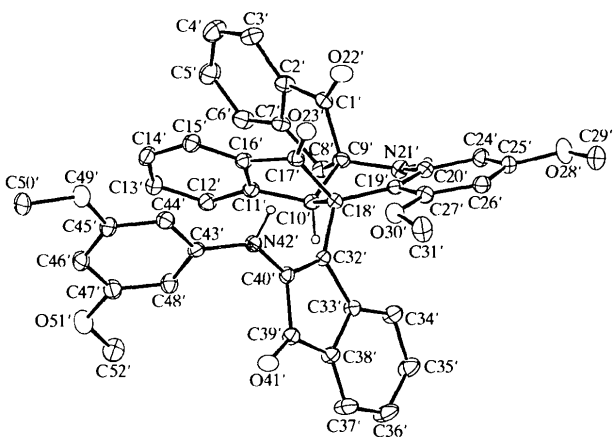

Fig. 3. The molecular structure of compound (4) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Compounds (3) and (4) exhibit both intra- and inter-molecular hydrogen bonding. The amino H atoms H42 [compound (3)] and H42′ [compound (4)] form intramolecular hydrogen bonds to O23 and O23′, respectively (H42···O23 2.30 Å and N42—H42···O23 137°, and H42′···O23′ 2.32 Å and N42′–H42′···O23′ 136°). The amino H21 and H21′ atoms form intermolecular hydrogen bonds to O41^i [symmetry code: (i) $1 - x$, $\frac{1}{2} + y$, $1 - z$] and O41′^{ii} [symmetry code: (ii) $1 - x$, $y - \frac{1}{2}$, $-z$], respectively (H21···O41^i 1.95 Å and N21—H21···O41^i 162°, and H21′···O41′^{ii} 1.99 Å and N21′—H21′···O41′^{ii} 173°).

Experimental

A solution consisting of 1,2-indanedione (0.20 g, 1.37 mmol) and 3,5-dimethoxyaniline (0.209 g, 1.37 mmol) dissolved in benzene (25 ml) was heated under reflux for 5 h. [Under these conditions 25 mg of the 1,2-indanedione was recovered. If heating were continued overnight the yield of compound (2) was increased to 185 mg (24%). There was also a dramatic decrease in production of compounds (3) and (4) to <5 mg.] The solution was then cooled and allowed to stand overnight. Thin-layer chromatography of this solution showed a complex mixture of highly colored products. The solvent was removed under reduced pressure and the crude material chromatographed on silica (eluent: 30% acetone/hexanes). Compound (2) was isolated as a blue–black solid (100 mg, 13%; R_f = 0.55; 30% acetone/hexanes) and recrystallized from this solvent. Compounds (3) and (4) co-crystallized as a diastereomeric pair and were isolated as an inseparable mixture (155 mg, 16%) which was recrystallized from CH_2Cl_2/hexanes.

Compound (2)

Crystal data

$C_{34}H_{28}N_2O_6$	Mo $K\alpha$ radiation
M_r = 560.61	λ = 0.71069 Å
Triclinic	Cell parameters from 254
$P\bar{1}$	reflections
a = 12.5262 (9) Å	θ = 2.82–25.35°
b = 12.8058 (7) Å	μ = 0.095 mm^{-1}
c = 10.2263 (5) Å	T = 200 (1) K
α = 100.762 (4)°	Flat needle
β = 110.156 (3)°	0.45 × 0.12 × 0.05 mm
γ = 110.603 (4)°	Blue–black
V = 1349.99 (16) Å^3	
Z = 2	
D_x = 1.379 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku R-AXIS IIc area-detector diffractometer	R_{int} = 0.029
φ oscillation scans	θ_{max} = 25.35°
Absorption correction: none	$h = -15 \rightarrow 15$
10 106 measured reflections	$k = -15 \rightarrow 15$
4464 independent reflections	$l = -12 \rightarrow 12$
3762 reflections with	Intensity decay: $\sim3\%$
$F > 2\sigma(F^2)$	(estimated from frame-to-frame scaling)

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.005
$R(F)$ = 0.061	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$wR(F^2)$ = 0.139	$\Delta\rho_{min}$ = -0.18 e Å^{-3}
S = 1.14	Extinction correction:
4464 reflections	SHELXL93 (Sheldrick,
492 parameters	1993)
All H-atom parameters refined	Extinction coefficient: 0.0100 (16)
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.8537P]$	Scattering factors from International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

Compounds (3) and (4)

Crystal data

$2C_{43}H_{34}N_2O_7 \cdot 2CH_2Cl_2$
$M_r = 1551.36$
Monoclinic
$P2_1$
$a = 7.9574$ (1) Å
$b = 19.4192$ (3) Å
$c = 24.2174$ (4) Å
$\beta = 91.406$ (2)°
$V = 3741.09$ (10) Å^3
$Z = 2$
$D_x = 1.377$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 420
reflections
$\theta = 2.52–25.35°$
$\mu = 0.23$ mm^{-1}
$T = 200$ (1) K
Flat needle
$0.45 \times 0.15 \times 0.05$ mm
Dark red

Data collection

Rigaku R-AXIS IIc area
detector diffractometer
φ oscillation scans
Absorption correction: none
29 922 measured reflections
7001 independent reflections
6613 reflections with
$F > 2\sigma(F^2)$

$R_{int} = 0.036$
$\theta_{max} = 25.35°$
$h = -9 \rightarrow 9$
$k = -23 \rightarrow 23$
$l = -29 \rightarrow 29$
Intensity decay: ~5%
(estimated from frame-to-
frame scaling)

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.161$
$S = 1.07$
7001 reflections
999 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 3.1440P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.019$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected torsion angles (°) in (3) and (4)*

	(3)	(4)
C10—C18—C32—C33	−65.1 (4)	68.4 (4)
C17—C18—C32—C33	−172.8 (3)	176.6 (3)
C19—C18—C32—C33	59.3 (4)	−56.0 (4)
C10—C18—C32—C40	112.5 (4)	−109.3 (4)
C17—C18—C32—C40	4.8 (5)	−1.1 (4)
C19—C18—C32—C40	−123.1 (4)	126.4 (4)
C32—C40—N42—C43	−128.4 (4)	123.4 (4)
C39—C40—N42—C43	61.3 (5)	−65.5 (5)
C24—C25—O28—C29	−2.8 (6)	−179.0 (4)
C26—C25—O28—C29	175.7 (4)	0.9 (6)
C46—C47—O51—C52	15.9 (6)	177.9 (4)
C48—C47—O51—C52	−164.7 (4)	−1.2 (6)

The least-squares refinement of compound (2) included isotropic refinement of all H atoms. The mean C—H bond distance was 1.00 Å, with a range of 0.95–1.07 Å. The mean standard uncertainty on C—H bond distances was 0.004 Å. In the least-squares refinement of compounds (3) and (4), the H atoms were treated using a riding model in which the coordinate shifts of the atom to which the H atom was attached were applied to the idealized H-atom bond lengths. In addition, for methyl H atoms the torsion angle was refined. Thus, there were 999 refined parameters [one scale factor + (nine parameters × 110 anisotropic atoms) + eight torsion angles].

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Black, D. St. C., Bowyer, M. C., Condie, G. C. C., Craig, D. C. & Kumar, N. (1994). *Tetrahedron*, **50**, 10983–10994.
Bullington, J. L. & Dodd, J. H. J. (1993). *Org. Chem.* **58**, 4833–4836.
Friedman, M. (1967). *Can. J. Chem.* **45**, 2271–2275.
Hauze, D. B., Petrovskaia, O., Taylor, B., Joullié, M. M., Ramatowski, R. & Cantu, A. A. J. (1998). *Forens. Sci.* **43**, 744–747.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1995). *BIOTEX. A Suite of Programs for the Collection, Reduction and Interpretation of Imaging-Plate Data.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Shapiro, R. & Chatterjie, N. J. (1970). *J. Org. Chem.* **35**, 447–450.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

4-*O*-Benzyl-2,3-*O*-isopropylidene-α-L-rhamnopyranose

LARS ERIKSSON,[a] PETER SÖDERMAN[b] AND GÖRAN WIDMALM[b]

[a]*Division of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and* [b]*Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden. E-mail: lerik@struc.su.se*

Abstract

It is shown that the title compound, $C_{16}H_{22}O_5$, has the α-anomeric configuration, a fact of interest for its use as an intermediate in oligosaccharide synthesis. One plausible intermolecular hydrogen-bond chain is found in the direction of the *b* axis.